Shock tube experimental and advanced computational investigations on pyrolysis of cyclohexane derivatives and $C_2 + C_2$ reaction

A Thesis
Submitted for the Degree of
Doctor of Philosophy
in the Faculty of Science

by
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Declaration

I hereby declare that the work presented in this Thesis titled **"Shock tube experimental and advanced computational investigations on pyrolysis of cyclohexane derivatives and C_2+C_2 reaction"** has been carried out by me at the Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India, under the supervision of Professor E. Arunan and Professor J. Gopalan.

Subharaj Hossain

April 2022

Subharaj Hossain

Certificate

We hereby certify that the work presented in this Thesis entitled **“Shock tube experimental and advanced computational investigations on pyrolysis of cyclohexane derivatives and C_2+C_2 reaction”** has been carried out by Mr Subharaj Hossain at the Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India, under our supervision.

April 2022 Professor E. Arunan and Professor J. Gopalan

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”Dearly precious to our hearts
Deep in us, but stands apart
This I love, of whom I speak
Him I see not, but Him I seek.”

SYNOPSIS

Every nation needs an affordable, accessible, and environmentally friendly energy source to secure and uphold a standard of living for its citizen. In India, the primary energy consumption grew by 7.9% in 2018 and is the 3rd biggest after China (23.6%) and USA (16.6%) with a 5.8% global share. Although there are significant research and development in renewable energies, more than 80% of current energies come from fossil fuels. For India, in the calendar year 2018, total primary energy consumption from coal, crude oil, natural gas, nuclear energy, hydroelectricity, and renewable power are 55.88%, 29.55%, 6.17%, 1.09%, 3.91%, and 3.40% respectively. Fossil fuels are produced by refining petroleum-based sweet crude oil. By refining, those fossil fuels, gasoline, diesel fuel, and jet fuel, are made with specific chemical and physical properties guided by the type of engine they will run. The composition of the fuel depends on the place where the fuel is refined, the overall composition of the fuel is presented by lumping the composition into several fuel classes. These fuel classes are the general group of fuel species with similar structures and chemical properties. Those are the following: n-alkane, iso-alkane, cycloalkane, aromatics, and others (include alkene and oxygenates). Among these, alkylcycloalkanes are important components of fossil fuels and account for around 10% in gasoline, 20% in jet fuel, and 27% in diesel.

In this thesis, we mainly focus on alkylcycloalkanes. Alkylcycloalkane can be generally classified into the following six groups: cyclopentane, cyclohexane, decalin, hydrindane, bicyclohexane, and other cycloalkane (cyclooctane and beyond). From the literature and the composition analysis of two fuels (JP-7(eq) and RP-1) performed in our lab using GC-MS, we found that cyclohexane can be categorized into different types: single side-chain alkylcyclohexane; multiple side-chain alkylcyclohexane. To understand initial decomposition, overall thermal decomposition and aromatic products formation from the fuel, it is essential to study the pyrolysis of different pure hydrocarbons belonging to these different classes. Chapter 1 of this thesis gives a brief introduction to fossil fuels, a literature review of the study of different alkylcycloalkane derivatives, and the key questions we will try to answer in this thesis. Chapter 2 details the shock tube, experimental setup, and computational methods used in the Thesis.

Chapter 3 discusses the pyrolysis of iso-propylcyclohexane. We have taken it as a typical example of single side-chain alkylcyclohexane. We have carried out a detailed theoretical study on the various possible reactions and associated intermediates/radicals involved in pyrolysis. State-of-the-art quantum chemical calculations have allowed us to probe the transition states for all the reactions and calculate the high-pressure rate constants. Theoretical calculation shows that the initial decomposition channel of iso-propylcyclohexane is the side-chain iso-propyl group elimination. We have also carried out experimental investigations using a single pulse shock tube. The pyrolysis experiments have been carried out for temperatures ranging from 923-1526 K and pressure ranging from 9.8–20.2 bar. Concentrations of all the major and minor products have been measured using GC-FID and GC-MS. The major products observed in the post-shock mixture have been the following: methane, ethene, acetylene, ethane, propene, allene, propyne, vinylacetylene, 1,3-butadiene, pentadiene, cyclopentadiene, and benzene. Experimental measurements have been used to validate the kinetic mechanism proposed in the theoretical study. We have used Chemkin for kinetic simulation. Simulation shows that benzene is mainly formed by the addition of resonance stabilized radicals like propargyl radical, allene, propyne, etc. and stepwise dehydrogenation of cyclohexane has a minor contribution (around 10%) towards benzene formation. Cyclohexyl radical (cC_6H_{11}) plays a key role in forming aromatic products (benzene, toluene, and styrene). We have proposed detailed kinetic models for the pyrolysis of iso-propylcyclohexane.

Chapter 4 discusses the pyrolysis of 1,3,5-trimethylcyclohexane. We have taken it as a typical example of multiple side-chain alkylcyclohexane. Here , we have also carried out both detailed theoretical study and experimental investigations using a single pulse shock tube. Theoretical calculation shows that the initial decomposition channel of 1,3,5-trimethylcyclohexane is the side-chain methyl radical elimination. The pyrolysis experiments have been carried out for temperatures ranging from 1017- 1542 K and pressure ranging from 13.35– 23.46 bar. The major products observed in the post-shocked mixture have been the following: methane, ethene, acetylene, ethane, propene, allene, propyne, 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, cyclopentadiene, benzene. Experimental measurements have been used to validate the kinetic mechanism proposed in the theoretical study. Simulation shows that stepwise dehydrogenation of cyclohexane has no contribution to benzene formation. It is mainly formed by the addition of resonance stabilised radicals/intermediates. Allene and dimethylcyclohexane radicals play key roles in the formations of aromatic products (benzene, toluene, and styrene). We have also proposed detailed kinetic models for the pyrolysis of 1,3,5-trimethylcyclohexane.

In Chapter 5, we report results from a detailed theoretical investigation of the thermal decomposition of decalin. We propose a detailed kinetic mechanism of its decomposition based on our calculations. Our calculation shows that the initial decomposition of decalin is the ring C-C bond opening. We also proposed the reaction mechanism of forming aromatic products like benzene, toluene, styrene, o-xylene, tetralin, and naphthalene. We have also calculated high-pressure limit rate parameters for all the elementary reactions.

Chapter 6 discuss results from a comprehensive state of art computational investigation of the $C_2 + C_2$ reaction. The addition of these pure carbon molecules is very important in combustion. Our calculation shows that the $C_2 + C_2$ reaction leading to $C_3 + C$, is not a barrier-less reaction, and it occurs via C_4 intermediate. We have calculated pressure-dependent rate parameters to determine the temperature and pressure conditions in which $C_2 + C_2$ leads to $C_3 + C$. Less than 500 K temperature and high pressure (pressure more than 10 bar) C_4 formation by addition of two C_2 dominates reaction in singlet surface. At a temperature of more than 500 K, reverse reaction of C_4 leading to C_2 dominates the reaction in singlet surface. However, formation of $C_3 + C$ dominates reaction at the triplet surface. Thus, $C_2 + C_2 \leftrightarrow C_4 \rightarrow C_3 + C$ reaction is sensitive to the spin state of C_2, and $C_2 + C_2 \rightarrow C_3 + C$ reaction at singlet surface is faster than triplet state.

Chapter 7 summarizes the results and conclusions from the work reported in the thesis.

In Appendix 1, we discuss about developing a sensor for calculating temperature and water concentration in combustion gases using tunable diode laser absorption spectroscopy (TDLAS). Using the HITRAN database and HITRAN Application Programming Interface (HAPI), we have simulated the water absorption spectrum using the Hartmann-Tran profile and selected a line pair suitable for high-temperature measurements. The Diode laser can be tuned using current and temperature controller for the suitable wavelength. We have used a photo diode as a detector. It is hoped that these results will be useful in future development of this technique.

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Chapter 1

Introduction, Motivation and Opportunities

1.1 Requirements of energy

Every nation needs affordable and environmentally friendly energy source to secure and uphold standard of living of its citizen. In India, the primary energy consumption grew by 7.9% in 2018 and is the 3rd biggest after China(23.6%) and USA(16.6%) with 5.8% global share[1]. Although, there are significant research and developments in renewable energies, more than 80% of current energies come from fossil fuels. For India, in the calendar year 2018, total primary energy consumption from coal, crude oil, natural gas, nuclear energy, hydroelectricity and renewable power are 55.88%,29.55%,6.17%,1.09%,3.91% and 3.40% respectively[1]. World wise energy demand is also increasing, especially among developing countries. Figure 1.1(a) shows that by 2040, energy consumption of India will increase by 9%[2] whereas figure 1.1(b) shows that world energy consumption rises nearly 50% between 2018 and 2050[3].

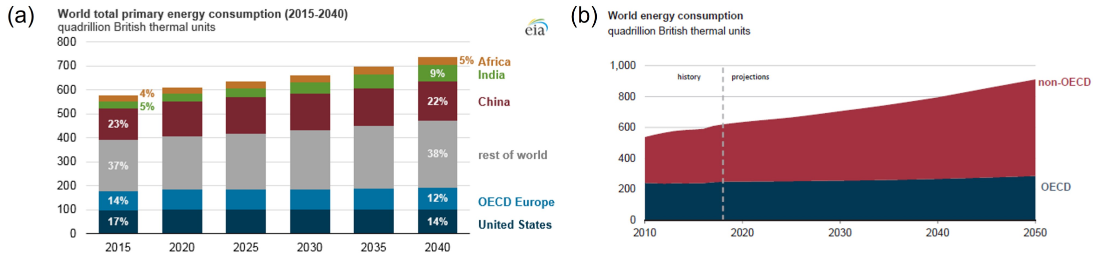

Figure 1.1: (a) World energy consumption by region (2015-2040)(figure adapted from reference 2). (b) World energy consumption (2015-2050)(figure adapted from reference 3. Source: U.S. Energy Information Administration (2021)).

The energy distribution has not changed so far in the last 50 years despite the increase of the energy consumption. Transportation is the largest single use of energy if electric power is factored out. Of total consumption, 97% transportation energy is derived from petroleum, whereas of total petroleum consumption, 44% is used for gasoline, 14% for diesel and 8% for aviation fuel[4].

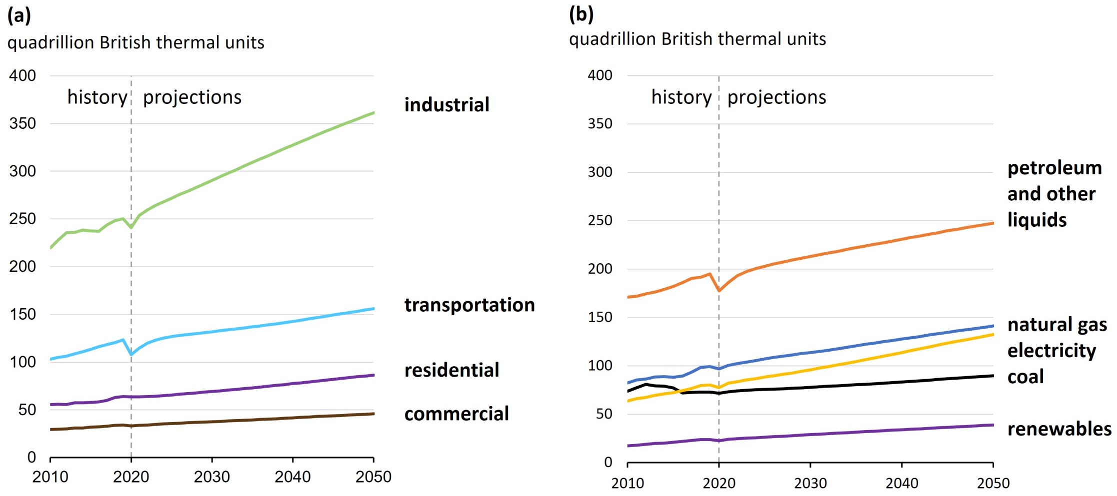

Figure 1.2: (a) World energy consumption by sector (2015-2050).(b) World energy consumption by fuel (2015-2050)(Figure adapted from reference 3. Source: U.S. Energy Information Administration (2021))

Figure 1.2 shows world energy consumption sector-wise and conresponding fuels[3]. These data suggest that transportation section has dominating role in energy consumption and efficient improvement of is transportation sector/ fossil fuels can have a large impact on the nation's energy use.

Like all other important part of our socity, energy use has some consequences. Impacts on environment is one of the significant consequences. Combustion of fossil fuel is the dominant source of air pollutants (e.g. CO_2 gas, unburnt hydrocarbons, smog soot, NOx, SOx etc. These emissions cause global warming, acid rains and also has health effects. While improvment of efficency of fossil fuels may not entirely solve these problems but clean, more efficient combustion—especially in internal combustion engines—is crucial to reducing the air pollutant emissions and also reducing the energy shortage.

1.2 Fossil fuel

Transportation fuels are produced by refining petroleum based sweet crude oil which can also be termed as fossil fuels. By refining those fossil fuels, gasoline, diesel fuel and jet fuel are made with specific chemical and physical properties guided by the type of engine they are going to burn. Diesel engines burn diesel fuel, spark-ignition(SI) engines burn gasoline, and gas turbine burns jet fuel and every engine is specific to work with the particular fuel but do not work with other type of fuels. Fossil fuels are very complex, multicomponent mixture of many hydrocarbons and other species, and composition varies in different parts on the world depending on where those fuels are refined. Hundreds of distinct hydrocarbon species are present in each gallon of the fuel. As composition of the fuel depends on the place where the fuel is refined, the overall composition of the fuel is presented by lumping the composition into several fuel classes[4]. These fuel classes are the general group of fuel species that have similar structures and chemical properties. One of such composition is shown in figure 1.4 in which the classes

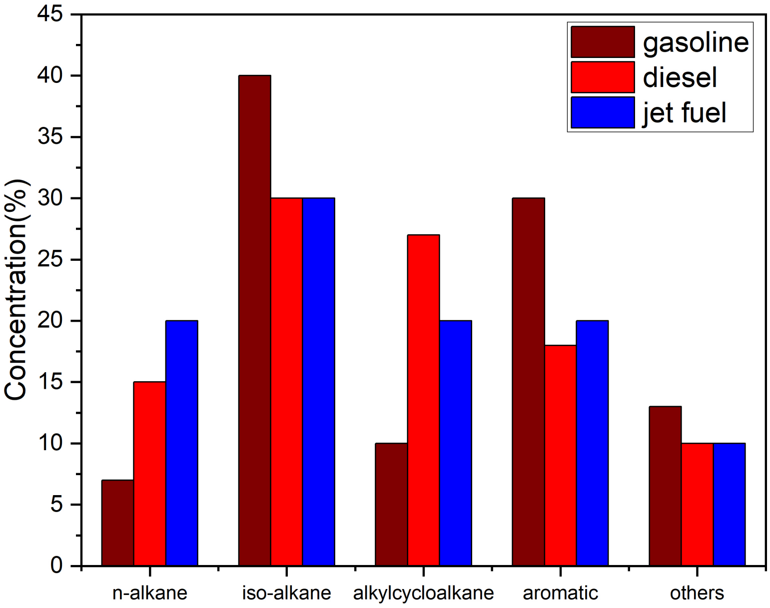

Figure 1.3: Level of different fuel class in conventional transportation fuel (reproduced from reference 4)

are the followings: **n-alkane** (n-paraffin), **iso-alkane**(iso-paraffin), **cycloalkane**, **aromatics**, and **others**(include alkene(olefin) and oxygenates). The presence of these composition at various fuels are shown in figure 1.3.

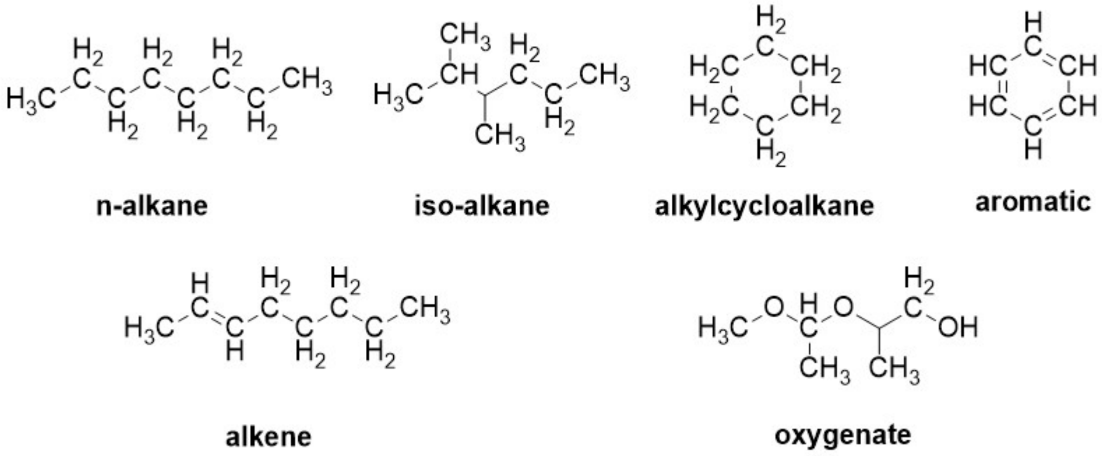

Figure 1.4: Typical molecules of major class of hydrocarbons

From these generalized fuel compositions, we can understand how the fuel burn on the different engines. Among these fuel classes, n-alkanes and cycloalkanes react rapidly and encourage knock whereas branched-alkanes react slowly and resist knock. Aromatic hydrocarbons on the other hand resist ignition and produce high level of soots.

Spark-ignition (SI) engine is used for gasoline burning, in which engine knock (sharp sounds caused by premature combustion of part of fuel) is important and here fuel/air mixture is slightly lean. So, in the gasoline, level of branched-alkane is high, but level of n-alkanes and cycloalkanes are low. As SI engine has spark ignition and lean premixed condition, presence of aromatics do not create soot formation. Thus gasoline contain high level of aromatics.

On the other hand, in both diesel and jet engine, there is no spark to initiate combustion as such the fuel must easily ignite. Thus, diesel and jet fuel contain high level of n-alkanes as well as cycloalkanes but level of branched-alkane is low. In diesel and jet engines, both fuel-lean and fuel-rich regions occur which can make aromatic hydrocarbon to produce large amount of soot easily. Thus diesel and jet fuel contain less amount of aromatic hydrocarbons.

As mentioned earlier, all those transportation/fossil fuels are produced from same sweet crude, petroleum-based oil. If crude oil is replaced by new source like oil sand, coal liquids, the overall composition of transportation fuel alter and these differences then lead to difference in physical properties as well as combustion performance and emission characteristics.

Among the newly proposed biofuel only ethanol is suited for SI engine[4]. Fuel from all other new source like oil sands, oil shale fuel, coal liquids, and most biodiesel fuel perform like conventional diesel fuel as they contain significant level of aromatics and cycloalkanes[4]. Each of the alternative fuel has its own unique feature or chemical signature. For example, biomass-derived fuels have high polymeric characteristics (from cellulose and lignins); oil sands fuels have high naphthenic content; oil and coal liquid fuels have more aromatic content than petroleum-based transportation fuels[4]. *A combination of theoretical, kinetic modeling and experimental studies will be required to develop an accurate understanding of their physical and combustion properties.*

1.2.1 Gasoline

Gasoline consists of hydrocarbon with C_4 to C_{12} carbon number with a density of 0.71–0.77 g/mL and boiling point of 303–463 K.

n-alkane is not found in large quantities in gasoline. Iso-alkane is generally found in large quantities with carbon number mainly ranging from C_4 to C_8. Common alkanes are n-butane, iso-butane, n-pentane, iso-pentane, and multiple methyl substituted hexane, heptane, and octane. Higher molecular weight alkane ($C_7 - C_8$) normally has one to three methyl substitution[5]. Cycloalkane found in gasoline are normally in the range of $C_4 - C_8$ which include the species like cyclopentane, methyl cyclopentane, cyclohexane, methyl cyclohexane and dimethyl cyclohexane isomer[5]. Olefin is also found in less quantity in gasoline. Typical olefins range from C_5 to C_8 and include linear and branched pentene and hexane isomers[5]. Aromatics normally has high molecular weight in gasoline and falls in the range of C_6 to C_9. Important aromatic species are the following: benzene, toluene, m-xylene, o-xylene, ethylbenzene and trimethyl benzene isomers[5]. In addition to these, gasoline also contain various oxygenates like methyl t-butylether(MTBE), ethyl t-butylether(ETBE) etc[5].

1.2.2 Diesel

Diesel is mostly hydrocarbons with 10 to 24 carbon numbers having a density of 0.81–0.86 g/mL and boiling point of 463–633 K[6]. It contains both n-alkane and iso-alkane. Iso-alkanes are slightly branched with one or two methyl substitution(s) on long chain. Cycloalkanes are primarily one-ring cyclohexane with multiple alkyl sidechains. Two-ring and larger cyclo-alkane are also present in little amount (less than 5% of the total fuel). Aromatics are primarily one-ring analogous (i.e., alkylbenzene) with little amount of substituted two-ring aromatics(naphthalene).

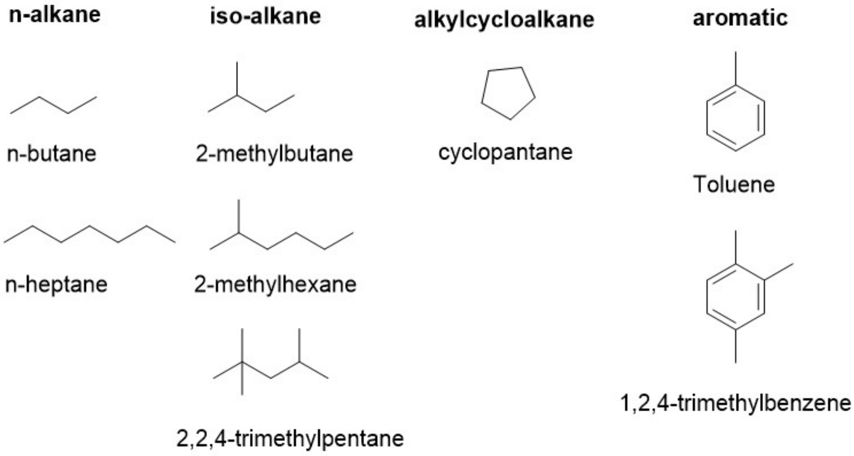

Figure 1.5: Representative molecular structures in gasoline fuels (figure is reproduced from reference 5).

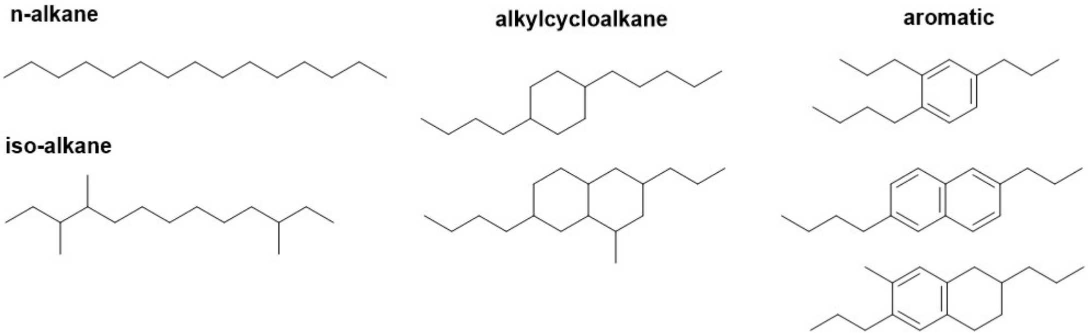

Figure 1.6: Representative molecular structures in desel fuels.

1.2.2.1 Diesel from direct coal liquefaction (DDCL)

In recent time, coal-to-liquids (CTL) technology has improved to produce alternative fuel of petroleum. CTL is the technology on the liquefaction of coal based on three basic approaches: pyrolysis, direct coal liquefaction (DCL)[7], and indirect coal liquefaction (ICL) and among those three approach DDCL is the product obtain from DCL[8]. Huang et al.[9] and Wang et al.,[10] analyzed detailed composition of DDCL using GCMS. In their analysis of the composition of DDCL it was found that DDCL approximately consists of 9.3% alkane, 88.1% cycloalkane and 2.6% aromatic by mass[9] which is very different from the composition of the conventional diesel.

1.2.3 Jet fuel

Jet fuel consists mainly of hydrocarbons with 8 to 16 carbon numbers having a density of 0.78–0.81 g/mL and boiling point of 433–553 K. The development and evolution of jet fuel has been described by Edwards et al.[11,12] in details and we give a brif description here. In the early 50's two fuels emerged, one is named $JP-4$ which is actually a "wide-cut" gasoline/kerosene mixture and the other one is a kerosene fuel with $–50^0$ C freezing point specified as $JetA-1$ in USA. Currently throughout the world civil aviation use $JetA-1$ except for the domestic carriers in the USA (which use Jet A having freezing point of -40^0C). In the 80's $JP-4$ is converted into $JP-8$ which is basically $JetA-1$ with a three additives (fuel system icing inhibitor, corrosion inhibitor/lubricity improver and static dissipater). During 2nd half of 2000's many special fuels were developed. $JP-5$ is a high flash kerosene used in US navy. $JP-6$ is a low-velocity kerosene developed for Mach 2+ aircraft, $JP-7$ is a low-volatile/high thermally stable, highly-processed (low sulfur and aromatic) kerosene developed for Mach 3 SR-71 aircraft. $JP-TS$ is a high thermally stable and lower freezing point fuel. $JP-9$ and $JP-10$ are high density missile fuels (not kerosene fuel) having properties like maximum volumetric energy content, clean burning, good low-temperature performance which consist only three hydrocarbons (methylcyclohexane, perhydronorbornadiene dimer, and exo-tetrahydrodicyclopentadiene) and one hydrocarbon (exo-tetrahydrodicyclopentadiene) respectively. $RP-1$ is the standard U.S. kerosene rocket propellant which has much narrow allowable density range and less amount of components like sulfur, alkenes and aromatics which cause deposits during regenerative cooling. $RP-2$ is basically $RP-1$ with ultralow amount of sulfur, and the physical properties for $RP-1$ and $RP-2$ are same[13]. $RP-3$ (China no. 3 aviation kerosene) is broadly used in China's aircraft industry and is similar to $JetA-1$[14].

Table 1.1: Typical aviation fuel Average composition (given in percentage)

	JP-4[12]	JP-5[12]	JP-7[12]	JP-8[12] (Jet A/A-1)	RP-1[12] (RP-2)	RP-3[15]
Alkane	59	45	65	60	39	53
Cycloalkane	29	34	32	20	58	37.7
Aromatic	10	19	3	18	3	4.6
Alkene	2	2	-	2	-	2
Sulfur, ppm	370	470	60	490	20(RP-1)	
others						2.7(alcohol)

1.2.3.1 GC-MS analysis of JP-7(equivalent) and RP-1

In our lab we have also analysed two jet fuel given by Defence Research and Development Laboratory (DRDL), Hyderabad, using GC-MS with DB-1 column. The GC-MS chromatogram are given bellow

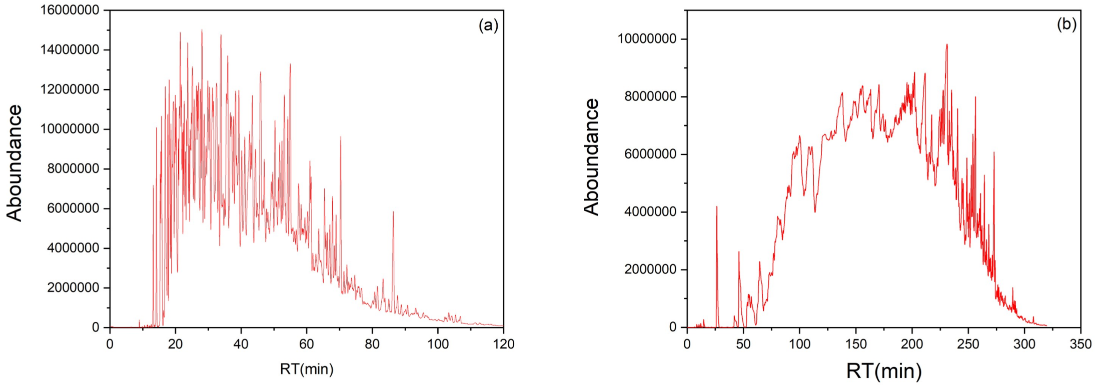

Figure 1.7: GC-MS analysis of (a)JP-7(equivalent) and (b)RP-1.

Table 1.2: Composition of JP-7(eq) and RP-1

	JP-7(eq)(mass%)	RP-1 (mass%)
Alkane	46.8	36.6
n-alkane	6.2	4.4
Iso-alkane	40.6	32.2
Cycloalkane	51.0	53.6
Aromatic	-	1.4
others	2.2	8.0

1.3 Surrogate fuel

As mentioned earlier, transportation/fossil fuels contain hundreds/thousands of individual hydrocarbons although the amount of each of the hydrocarbon varies from place to place that make it impossible to carry out repeatable experiments with real fuel (as for fundamental modelling and experimental studies a fixed chemical composition is needed). To do that one approach is to mimic real fuel with a definite chemical composition mixture which are called "surrogates" for the fossil fuels. Fuel surrogates can be two types,

i)**Physical surrogate:** a mixture that has the same physical properties (vaporization, density, viscosity, surface tension, diffusion coefficient, etc.) as the fuel to be studied. For example, dodecane($C_{12}H_{26}$) has physical properties like JP-7 over the 366-922 K temperature range.

ii)**Chemical surrogate:** a mixture that has the same chemical properties (flame speeds, ignition properties, molecular weight, C/H ratio, adiabatic flame temperature, pollutant formation, etc.) as the fuel to be studied. The mixture generally has the similar chemical-class composition and average molecular weight as the fuel, such as the right proportion of alkane, cycloalkane, aromatics etc. Although surrogate would not be properly able to simulate those fuel chemistries which depend on the trace species, like thermal-oxidative stability (dependent on ppm level of trace heteroatom and metal species), pollutant or soot emissions (depends on trace fuel species).

The procedure for developing surrogate mixture have been described elsewhere[13] and is briefly described here. The procedure is the following:

a) Identify the chemical composition of fuel by chemical analysis.

b) making a list of candidate molecule from the analysis of fuel which represent the various chemical class of hydrocarbon (n-alkane, iso-alkane, cycloalkane, aromatic etc.

c) Development of an equation of state, a viscosity surface and a thermal conductivity surface of those individual pure-fluid candidate molecule and use of a mixture model to incorporate the pure-fluid equations for both thermodynamic and transport properties.

d) Choice of surrogate mixture and their composition by determining the composition that minimizes the difference between the predicted and experimental data for the distillation curve, density, sound speed, viscosity, and thermal conductivity.

In summary, the motivation for surrogate fuels is to simulate combustion behaviors of fossil fuels. These surrogates are selected mostly based on five criteria:

i) limit of 10-15 hydrocarbon,

ii) match compound class in fuel,

iii) match distillation curve in fuel,

iv) high purity and

v) minimum cost.

A good example of a chemical surrogate is the surrogate of JP-8 developed by Violi et al.[16], which is the mixture of 6-10 compounds (iso-octane, methylcyclohexane, m-xylene, toluene, etc) and it properly reproduces the kinetic properties, (sooting, flame structure and oxidation in flow systems), as well as the physical properties (volatility, boiling curves, and flash point) of actual JP-8 fuel. Several surrogates have been proposed for gasoline, diesel and all types of jet fuels, and have been reviewed in various publications[5,6,11,12]. We have summarized all these in next section.

1.3.1 Gasoline surrogates

Pits et al.,[17] in their publication developed experimental database for surrogate gasoline fuels. They recommended initially three component mixtures for gasoline surrogate: n-heptane, iso-octane, and toluene.

For further refinement they suggested to add more components and for that they recommended diisobutylene and methylcyclohexane.

1.3.2 Diesel surrogates

Farrell et al.[18] in their work proposed surrogates in diesel fuel's surrogate development. They suggested two tier plans for rapid progress and developing surrogate fuel model,

i) Tier 1: n-decane, iso-octane, methylcyclohexane and/or toluene.

ii)Tier 2: n-hexadecane, heptamethylnonane, n-decylbenzene, and 1-methylnaphthalene.

Tier 1 consists of molecules for which mechanistic data are already available whereas for tier 2 molecules, large amount of work is required to develop the database and mechanistics understanding.

1.3.2.1 DDCL surrogates

Huang et al.[9] proposed surrogate mixture of DDCL after analysis of the composition of DDCL. Their proposed surrogate candidates are the following compound: n-hexadecane, iso-cetane, decalin, n-butylcyclohexane, bicyclohexyl, and toluene.

1.3.3 Jet fuel surrogates

Edwards et al.[12] in their work summarized proposed surrogate mixture of JP-4, JP-5, JP-8, and RP-1. Tables 1.3, 1.4, 1.5, and 1.6 summarize all the surrogates.

Huber et al.[13] also proposed surrogate mixture for the thermophysical properties for RP-1 and RP-2. Their proposed mixture is listed in table 1.7.

Table 1.3: Surrogate of JP-4

Compound	(vol%)	Compound	(vol%)
n-hexane	5.5	n-nonane	10
cyclohexane	8	cyclooctane	8
n-heptane	8	n-decane	10
methyl cyclohexane	8	decalin	5
toluene	8	tetralin	1
n-octane	8	n-dodecane	10
1-methyl naphthalene	0.5	n-tetradecane	10

Table 1.4: Surrogate of JP-5

Compound	(vol%)	Compound	(vol%)
n-decane	2.5	n-pentylcyclohexane	11
decalin	11.5	1,3-diiopropylbenzene	3
tetralin	9.5	1-phenyl hexane	5
n-dodecane	25	n-tridecane	10
1-methyl naphthalene	1.5	n-heptylcyclohexane	11
n-tetradecane	5	n-pentadecane	5

Table 1.5: Surrogate of JP-8

Compound	(vol%)	Compound	(vol%)
methyl cyclohexane	5	n-tetradecane	15
Iso-octane	5	m-xylene	5
cyclooctane	5	Butyl benzene	5
n-decane	15	1,2,4,5-teramethyl benzene	5
tetralin	5	Hexadecane	10
n-dodecane	20	1-methyl naphthalene	5

Jia-Qi et al.[19] and Dong et al.[15] proposed surrogates of RP-3 after analysis of the composition of RP-3 using GC-MS in their work. Jia-Qi et al.[19] proposed three components mixture:

n-dodecane/ 1,3,5-trimethylcyclohecane/ n-propylbenzene (73.0%/ 14.7%/ 12.3%, mass fraction);

Table 1.6: Surrogate of RP-1

Compound	(vol%)	Compound	(vol%)
n-undecane	4.7	n-hexylcyclopentene	2.7
n-dodecane	6	n-heptylcyclopentane	3.6
n-tridecane	18.8	n-octyl cyclopentane	11.2
Dimethylnaphthalene	4	n-nonylcyclopentene	7.5
n-tetradecane	12.5	Bicycloparaffin 1 (C11H20)	11.3
Pentamethyl Benzene	1.3	Bicycloparaffin 2 (C12H22)	14.7
Hexamethylbenzene	1.7		

Table 1.7: Surrogate of RP-1 and RP-2 (adopted from reference 19)

Compound	RP-1(mole fraction)	RP-2(mole fraction)
α-methyldecalin	0.354	0.354
5-methylnonane	0.15	0.08
2,4-dimethylnonane	0	0.071
n-dodecane	0.183	0.158
heptylcyclohexane	0.313	0.333

whereas Dong et al.[15] proposed four components mixture:

n-decane/ n-dodecane/ ethycyclohexane/ p-xylene (40%/ 42%/ 13%/ 5% ,molar fraction).

1.4 Alkylcycloalkane

As mentioned before (figure 1.3) alkylcycloalkanes are important components of fossil fuels and account for around 10% in gasoline, 20% in jet fuel and 27% in diesel.

Again, among the jet fuels cycloalkanes content in Jet-A, JP-4, JP-5, JP-7, JP-8, RP-1, and RP-3 are respectively ∼ 3.3%[20], ∼ 29%, ∼ 34%, ∼ 32%, ∼ 20%, ∼58%[12] and ∼ 38%[15]. In our analysis of JP-7(equivalent) and RP-1 cycloalkane contain respectively ∼ 51%, and 54%.

Cycloalkane content is much large for new transportation fuel source. e.g., Diesel from direct coal liquefaction (DDCL) contain 88.1%[9] of cycloalkane. Diesel from oil sands also have higher fraction of cycloalkane[21]. From the previous section for the discussion of transportation fuel composition, proposal of different

Table 1.8: Presence of different classes of alkylcycloalkane in different fuel (given in percentage). * our analysis.

alkylcycloalkane	JP-7* (eq)	RP-1*	DDCL[9]	DDCL[10]	RP-3[14]
cyclopentane	-	14	-	-	-
cyclohexane	64	21	8	14	85
Decalin	29	39	72	65	15
Hydrindane	1	5	8	15	-
bicyclohexyl	1	-	9	6	-
others	5	21	2	-	-

surrogates and from our analysis of JP-7(eq), RP-1 compositions, we can even classify different cycloalkanes. Cycloalkanes can be generally classified into the following six groups: cyclopentane, cyclohexane, decalin, Hydrindane (octahydro-1H-Indene), bicyclohexyl, and other cycloalkane (cyclooctane and beyond).

Table 1.8 shows the percentage of different classes of alkylcycloalkane in different fuels. Figure 1.8 shows the molecular example of all classes of alkylcycloalkane.

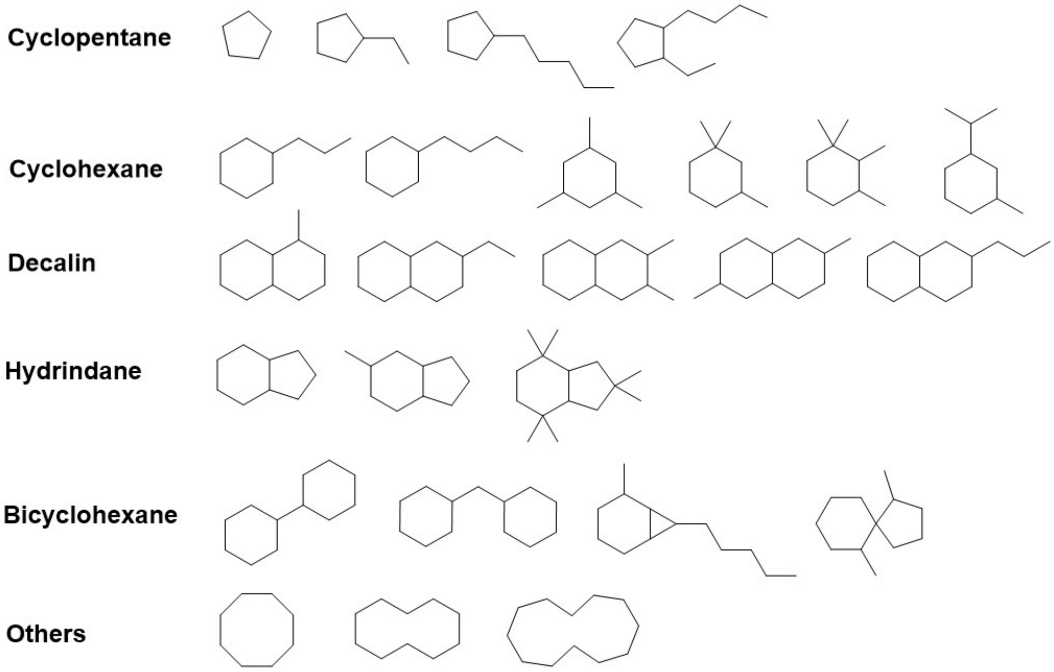

Figure 1.8: Example of all classes of alkycycloalkane.

From the above table, we can see that cyclohexane and decalin group are the two major groups of cycloalkanes. Cyclohexane is more abundant for conventional fuel like JP-7 while decalin is more abundant for new type of fuel like DDCL. Due to above fact, for cycloalkane class, cyclohexane and alkyl-cyclohexanes (e.g., methylcyclohexane, ethylcyclohexane, n-propylcyclohexane, and n-butylcyclohexane) are selected as model compounds. Cyclohexane is used as a basic kinetic model for cycloalkane while methylcyclohexane/ethylcyclohexane kinetic model is used to represent long side-chains cycloalkane. Due to recent time development of decalin kinetic model, its also used as a surrogate for cycloalkane. From our analysis of JP-7(eq), we find two types of cyclohexane,

i)single side-chaines alkylcyclohexane and

ii) multiple side-chains alkylcyclohexane.

Similar classification can also be done for decalin.

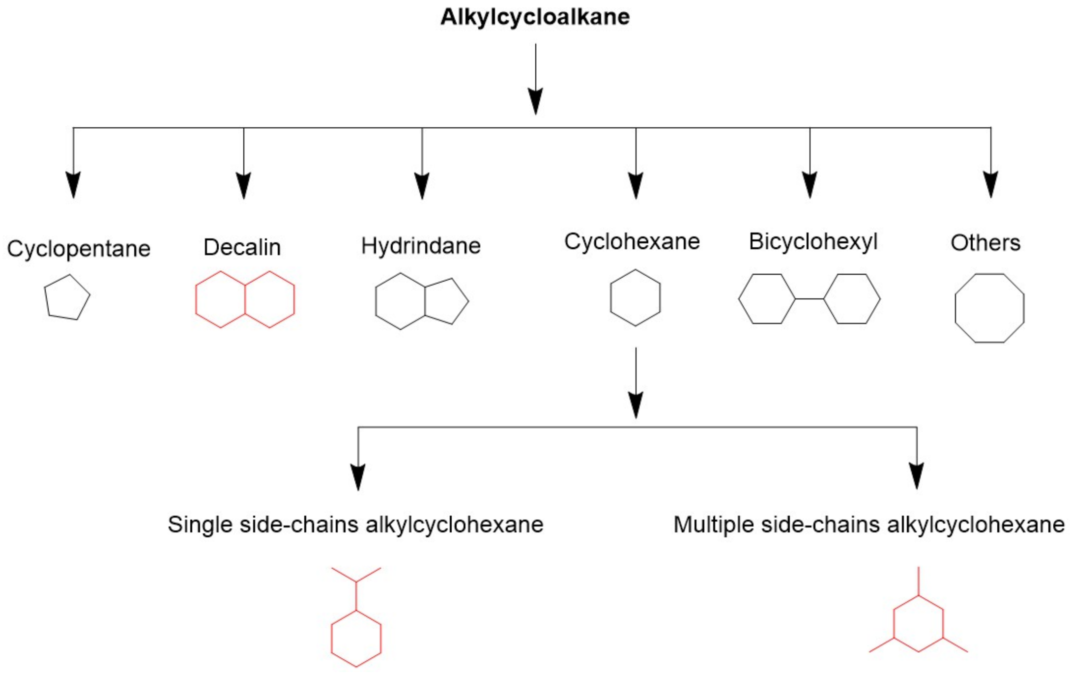

Figure 1.9: Alkylcycloalkane tree.

Among alkylcycloalkane, cyclohexane has been studied extensively as it is an important surrogate component and its reaction mechanism is the basis for understanding the combustion properties of alkylcyclohexanes. The literature of cyclohexane combustion is very rich and it covers theoretical (reaction pathways and rate constant calculations), experimental studies (pyrolysis, oxidation, flame), and kinetic modeling[22–32]. Study of alkylcyclohexane beyond cyclohexane is quite limited. Literature review of theoretical and experimental studies on alkylcyclohexane and decalin are listed in the table 1.9.

From these literature, we can find few important questions which need to be answered for alkylcycloalkane (and is also discuss in detail in reference 14).

i) Scarcity of theoretical studies of thermal decomposition of alkylcycloalkane: From the table 1.9, we can see that very few literature reports are available for the theoretical thermal decomposition for alkylcycloalkane beyond methylcyclohexane. Most of the cases, initial decomposition reaction, isomerization, H-atom abstraction, radical decomposition, and other reactions are estimated from the reaction associateed with small species that have some sort of functional similarity which can associate with significant errors.

ii) Initial decomposition mechanism of alkylcycloalkanes: Initial decomposition channel of alkylcycloalkane is an important step for the thermal decomposition/combustion for alkylcycloalkane. It is known that alkylcycloalkane decomposition either starts by ring opening to form alkene or dissociation of the side-chain alkyl group to form alkylcycloalkane radical and the competition between those two steps has significant effect on the whole decomposition mechanism as well as on the formation of the aromatics. Ring opening to form alkene goes via a biradical intermediate which is multireference in character. Again, dissociation of the side-chain alkyl group form two radical products, potential energy surface associate to the dissociation can have significant multireference character. That's why multireference method is needed for theoretical study of these initial decomposition step which is missing in the literature beyond methylcyclohexane for the case of alkylcyclohexane and so far, no such kind of study is available for decalin too.

iii) Aromatic formation pathways during alkylcycloalkane combustion: The first aromatic ring is considered as the rate controlling step to form polycyclic aromatic hydrocarbons and soot. Benzene formation is proposed mainly in two ways: a) combination of resonance stabilized radicals (e.g., $C_5H_5 + CH_3$, isomerization of fulvene etc.), b) stepwise dehydrogenation of cyclohexane. Toluene is mainly formed by stepwise dehydrogenation of methylcyclohexane. Although previous studies addressed benzene formation pathways in cycloalkane combustion, the reaction mechanism has not been fully clarified, and the effect of the multiple side-chains, single side-chain, and the length of side-chain of alkylcyclohexane on aromatic formation is not clear.

iv) Scarcity of experimental and kinetic modeling studies of alkylcycloalkane pyrolysis in high pressure and high temperature: Table 1.9 shows that previous studies mainly focused on the oxidation and addressed the macroscopic properties of cycloalkane (e.g., ignition delay time, laminar flame speeds etc.). Experimental data in a high-pressure pyrolysis process without the participation of oxidation

Table 1.9: Literature review

alkyl-cycloalkane	Experiment /Theory	Temperature (K)	Pressure (atm)	Type of study	Ref
Single side-chines alkylcyclohexane					
Methyl-cyclohexane	ST oxidation	1250-2100	1-4	IDT	33
	RCM oxidation	680-980	10-20	IDT	34
	RCM oxidation	680-905	15.1,25.5	IDT	35
	ST oxidation	881-1319	10.8-69.5	IDT	36
	Engine oxidation	750-860	10-25	Speciation	27
	Premixed flame	Flame temp. profile	0.04	Speciation	37
	Premixed flame	353 (unburnt gas temp.)	1-10	LFS	29
	HTF Pyrolysis and combustion	842-1721	0.04,0.2, 1.0	Speciation	38
	ST pyrolysis	850-1650	39.5,98.7	Speciation	39
	JSR oxidation	500-1100	, 197.4,1	Speciation	40
	QCC pyrolysis	800-2000	0.01, 0.04, 0.2,0.4, 1.0, 10, 100, HPL	Rate constant for initial decomposition reaction	41
	QCC pyrolysis	298-2000	HPL	Rate constant for all elementary reaction	42
Ethylcyclohexane	ST oxidation	881-1319	10.8-69.5	IDT	36
	Premixed flame	353 (unburnt gas temp.)	1-10	LFS	29
	JSR oxidation	500-1100	1.05	Speciation	43
	HTF Pyrolysis and combustion	900-1550	0.04,0.2 ,1.0	Speciation	44

alkyl-cycloalkane	Experiment /Theory	Temperature (K)	Pressure (atm)	Type of study	Ref
Single side-chines alkylcyclohexane					
	HTF Pyrolysis	900-1300	1	Speciation	[45]
	QCC oxidation	500-1100	HPL	Rate constant for all elementary reaction	[46]
	JSR oxidation	480-780	1	Speciation	[47]
	ST oxidation	1110-1650	1	IDT	[48]
	ST oxidation	1000-1700	1.1-10	IDT	[49]
n-propyl-cyclohexane	JSR oxidation	950-1250	1	Speciation	[50]
	RCM oxidation	620-930	4.5-13.4	IDT, Speciation	[51]
	Premixed flame	353(unburnt gas temp.)	1	LFS	[52]
	Premixed flame	Flame temp. profile	0.066	Speciation	[53]
	ST oxidation	1110-1650	1	IDT	[48]
	FR pyrolysis	950-1300	0.4,1	Speciation	[54]
	FR, JRS, ST and RCM oxidation	550-1200	8, 20, 40	IDT, Speciation	[55]
Iso-propyl-cyclohexane	FR pyrolysis	880-1340	0.4,1	Speciation	[56]
n-butyl-cyclohexane	Premixed flame	353 (unburnt gas temp.)	1	LFS	[52]
	FR oxidation	600-820	8	Speciation	[57]
	ST oxidation	1280-1480	1.5-3	IDT	[58]
	ST oxidation	707-1458	2,5,15	IDT	[59]
	RCM oxidation	612-1374	10, 15, 20	IDT	[60]

alkyl-cycloalkane	Experiment /Theory	Temperature (K)	Pressure (atm)	Type of study	Ref
Single side-chines alkylcyclohexane					
n-butyl-cyclohexane	FR oxidation	650-1075	1,10, 15, 20	IDT , Speciation	61
	ST, RCM oxidation	630-1420	10,30,50	IDT	62
	QCC	800-2100	HPL	Rate constant for elementary reaction	63
Multiple side-chines alkylcyclohexane					
1,4-dimethyl-cyclohexane	FSR pyrolysis	767-835	0.01	Speciation	64
1,3-dimethyl-cyclohexane	ST oxidation and pyrolysis	1049-1544	3-12	IDT	65
1,2-dimethyl-cyclohexane	QCC	300-2500	HPL	Rate constant for elementary reaction	66
1,3/1,2-dimethyl-cyclohexane	Motor engine	428 (intake temp.)	48	Ignition process	67
1,3-dimethyl-cyclohexane	ST	1100-1200	2.5	Isomerization Rate parameter	68
1,2,4-trimethyl-cyclohexane	JSR oxidation	600-1100	1	Speciation	69
1,2,4-trimethyl-cyclohexane	FR pyrolysis	775-1200	0.04, 1	Speciation	70
Two fused cyclohaxane ring					
Decalin	QR pyrolysis	973-1223	0.5	Speciation	71
	Pyrolysis	1093	1.78	Speciation	72
	QR pyrolysis	1053, 1073	1	Speciation	73
	FR pyrolysis	973-1123	1	Speciation	74
	TF pyrolysis	1083	1, 2	Speciation	75

alkyl-cycloalkane	Experiment /Theory	Temperature (K)	Pressure (atm)	Type of study	Ref
Decalin	TR pyrolysis	1083	1	Speciation	76
	Conventional pyrolysis	770-1020	1	Speciation	77
	FR Pyrolysis	698-748	23-75	Speciation	78
	Reactor pyrolysis	1083	3.95	Speciation	79
	FR pyrolysis	920-1500	0.04, 0.2, 1	Speciation	80
	FR pyrolysis	700-810	20-100	Speciation	81
	ST oxidation	1060-1290	0.6-1.5	IDT	82
	ST oxidation	993-1305	9-48	IDT	83
	FR oxidation	600-800	8	CO production	84
	FR oxidation	626-731	8	CO production	85
	Motored engine oxidation	750-950	5-17	Speciation	86
	ST oxidation	769-1202	11.7-51.2	IDT	87
	FR oxidation	500-2200	0.0395	Speciation	88
	QCC	700-1500	HPL	PES for aromatic product formation	89
	QCC	200-2000	0.001-100	Rate parameter for H-abstraction reaction by OH radical	90
Note: ST- Shock tube; IDT- ignition delay time; RCM- Rapid compression machine; LFS -laminar flame speed; HTF-high temperature furnace; QCC- quantum chemical calculation; HPL- high pressure limit; FR- Flow reactor; QR- quartz reactor; TF- Tubular furnace; TR- Tubular reactor; PES- Potential Energy Surface; FSR- Flow stirred reactor					

reaction with detailed speciation were seldom reported. To study unimolecular decomposition pathway and the reaction mechanism for aromatics, pyrolysis environment is suitable. Again, compared to alkane, the kinetic models for alkylcycloalkane are not well developed, and well validated kinetic models are required for alkylcycloalkane pyrolysis.

1.5 Scope of the current work

As we have discussed above, one common approach to development of surrogates for practical fuels is to take advantage of the same fuel classes already described above. The key is to have one or more representatives of each of those classes with detailed chemical kinetic reaction mechanisms with validation by experimental data. Some of the classes, such as the n-alkanes and iso-alkanes have numerous examples with validated mechanism, while the cycloalkanes and aromatics have only few studies avalable. As per the discussion of "Basic Research Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels" [4] due to the lack of detailed mechanism and reaction pathways for most of the components of these fuels, kinetic modeling are lacking for currents transportation fuels. As most of the combustion environments involve high pressure, as high as 100 bar for diesel application and perhaps as high as 1000 bar in specialized systems in future[4]. So, there is need for both experimental studies and theoretical studies at high pressure which is seriously lacking. Virtually no elementary reaction rates have been measured for hydrocarbons with more than six or seven carbon atoms. Most of the cases, initial decomposition reaction, isomerization, H-atom abstraction, radical decomposition, and other reactions are estimated from the reaction associate small species that have some sort of functional similarity (e.g., methane, ethane, propane, n-butane, iso-butane etc. for alkanes; cyclohexane, methylcyclohexane for alkylcyclohexane). The data that have been used to estimate the rates of similar reaction for large species, may have limitless error which is difficult to assess. For that reason, it is important to study detailed reaction mechanism for large hydrocarbon species of importance to transportation fuels directly.

Very little experimental, theoretical, or kinetic modeling information is available at any temperature or pressure for alkylcycloalkane species. This gives the main motivations for the present study. In this thesis, we have developed reaction mechanism of trimethylcyclohexane(multiple side-chins alkyl cyclohexane) and isopropylcyclohexane(single side-chines alkyl cyclohexane) pyrolysis from experiments as well as high-level quantum chemistry calculations and detailed kinetic modeling which is validated by experimental results.

a) Shock tube has been used as a reactor for the pyrolysis while GC-FID-FID and GC-MS have been used for identifying and quantifying the post pyrolysis products.

b) All the important reaction pathways during pyrolysis have been calculated using various electronic structure theory and the corresponding rate constants have been calculated based on transition state theory (TST) and variational transition state theory (VTST).

c) Finally based on literature data and calculated reaction pathways, a detailed pyrolysis model for of trimethylcyclohexane and iso-propylcyclohexane have been developed and has been validated by our experimental data. For decalin, only step b has been done i.e., only theoretical calculation of important elementary reaction and corresponding rate parameters evaluation.

Thesis organization:

Chapter 2: Experimental and Computational Methods
Chapter 3: Iso-propylcyclohexane pyrolysis at high pressure and temperature
Chapter 4: 1,3,5-trimethylcyclohexane pyrolysis at high pressure and temperature
Chapter 5: Theoretical Kinetic Study of Thermal Decomposition of Decalin
Chapter 6: Computational investigation on $C_2 + C_2$ addition reaction: importance of spin state in combustion
Chapter 7: Conclusions
and
Appendix A: Development of a sensor for calculating temperature and water concentration in combustion gases using a single tunable diode laser

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Chapter 2

Experimental and Computational Methods

2.1 Experimental Method

In the kinetic study(pyrolysis/combution), shock tube has been extensively used as a reactor for its usefull features[1]. In a normal reactor,for high-temperature gas reactions, the gas is heated by contact with a hot surface and gas temperature is increased to the required temperature in a finite time whereas in a shock tube the heating occures instantly without wall effects. In addition to this, in a shock tube the cooling rates of heated gas generally falls in the range of 0.5 to 5 K per μs. Thus, very well defined short reaction times (few milliseconds) can be achieved using shock tube for the study of kinetic reaction rates. Thus it is also known as milliseconds high-temperature furnace[2]. For these reasons, in a shock tube chemical reaction/process can be studied at a given temperature without the effect of surface reaction, secondary reactions or process occuring at intermediate temperatures.

2.1.1 The Shock Tube

The shock tube is a long cylindrical tube of a fix internal diameter divided into two parts (driver section and driven section) by a metalic diaphragm[1] (figure 2.1). The high-pressure side is known as the driver section and the low-pressure side is referred to as the driven section. The shock tube generates shock wave by the sudden bursting of the diaphragm by increasing the pressure in the driver section. After the bursting of the diaphragm, a compression wave (adiabatic compression, heating process) is formed in the low-pressure gas region (driven section) which leads to form a **shock front**. At the same time, an expansion/rarefaction wave (adiabatic expansion, cooling process) travel back into the driver section.The driven gas (experimental gas) and driver gas make contact at **contact surface** which moves rapidly along the tube behind the shock front. The temperature increases from the initial room temperature to high value at shock front, remains steady upto the contact surface, then its falls rapidly below room temperature, and then in the expension wave rises again to the initial temperature.

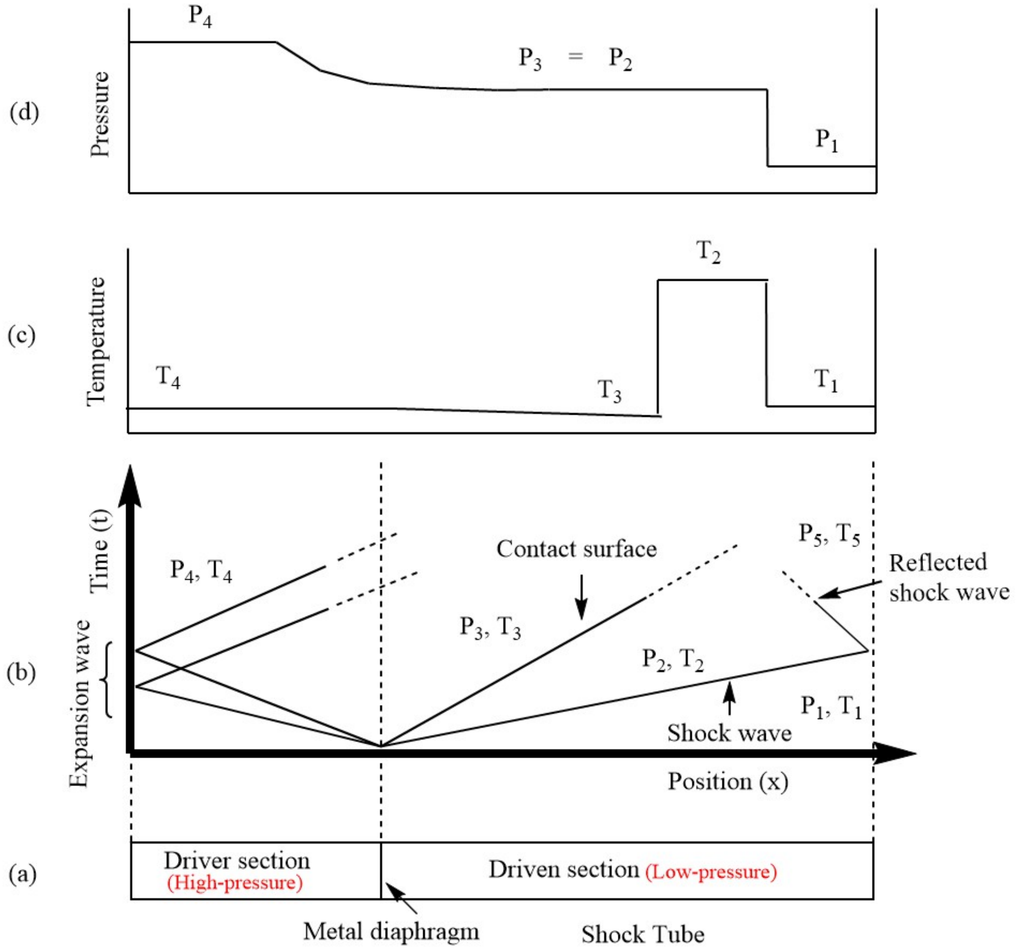


Figure 2.1: (a) Shock tube (b) The x-t diagram of shock/expansion wave propagation applicable for the shock tube (c) The temperature distribution (d) The pressure distribution

As per the convention, the pressure and temperature of different regions are denoted as: P_1 , T_1 at initial low-pressure region ; P_2 , T_2 at region between the shock front and contact surface; P_3 , T_3 at region between the contact surface and expansion wave; and P_4 , T_4 at the high-presssure side. In the normal shock tube $T_4 = T_1$ usually. If the shock wave gets reflected at the end of the tube, temperature and pressure further increase, and those are denoted as P_5 , T_5.

2.1.2 Experimental setup used in present study

Single pulse Chemical Shock Tube 1 (CST-1) has been used to carry out experiments discussed in the present thesis. It's an aluminium tube of 50 mm internal diameter and 25 mm wall thickness. The length of the driver section is 1.8 m and that of the driven section is 3.3 m. A dump tank of diameter 100 mm having a length of 1.6 m is connected near to the diaphragm station in the driven section at an angle of 45^0 to the shock tube. Aluminium diaphragm (1 mm thickness) was scored before placing it between the driver and driven sections. The driven section has been further divided into two sections with the placing of a ball valve 0.4 m before the end wall (sample chamber). The pressure profiles inside the shock tube are obtained by PCB pressure transducers (model no. 113B22) fitted at specific locations in driven section. Temperature has been calculated from normal shock relations using the measured Mach number (obtained from PCB sensors placed at 0.57 m apart). A Tektronix (model no. TDS-2014B) oscilloscope has been used to record the pressure signals. The reaction time has been obtained from the pressure sensor mounted at 0.5 mm from the end wall.

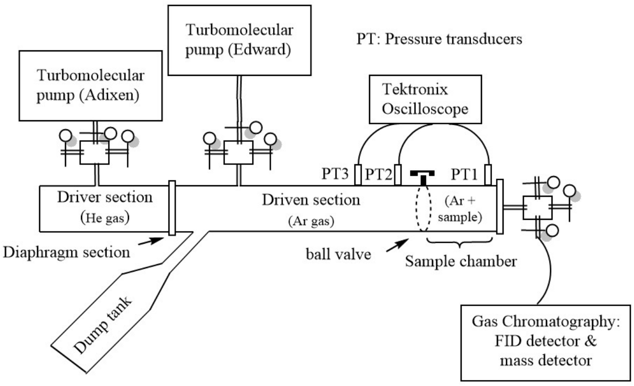


Figure 2.2: Schematic of the single pulse shock tube (CST-1)

Reaction time is the time duration in which reflected shock wave survives before it is quenched due to the arrival of expansion wave and is also known as dwell time. Edward (TCI pumping station) turbomolecular vacuum pump has been used to evacuate the driven section while the driver section has been evacuated using an Adixen (ATP 400) turbo molecular vacuum pump. Helium (99.999 % pure) has been used as driver gas and Argon (99.999 % pure) as driven gas. The sample-chamber containing the sample and argon mixture has been maintained at 343

K during the experiments to prevent condensation of the gaseous sample and the products. The schematic diagram of CST-1 can be seen in figure 2.2.

2.1.3 Operation of the shock tube

As mentioned before, an aluminum diaphragm kept at the diaphragm station has been used to separate the driver and the driven sections. The aluminum diaphragm (figure 2.3) which is a circular aluminum metal sheet of 1 mm thickness has been scored to different thickness to obtain different reflected temperatures behind shock.

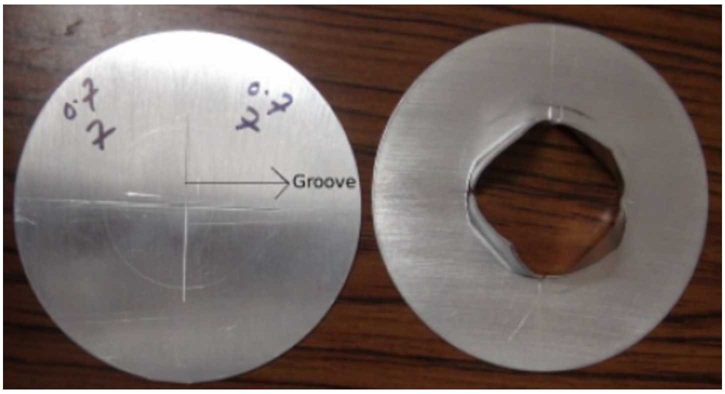
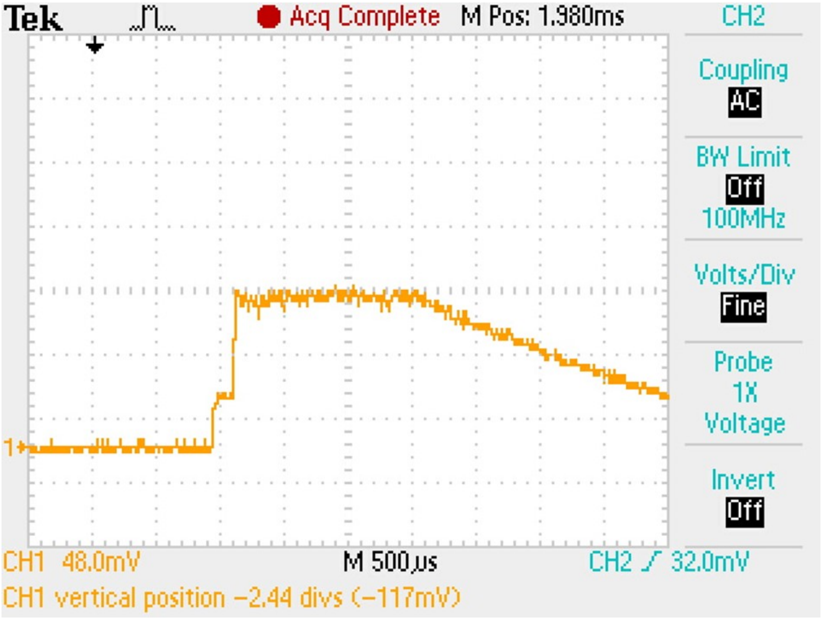


Figure 2.3: Aluminium diaphragm. Left: Before experiment. Right: After experiment.

Before the evacuation, the shock tube has been closed with a diaphragm in between the driver and driven section. Then, driven section have been evacuated using turbomolecular pump (Edward, TCI pumping station) upto 10^{-6} Torr. Then the evacuated driven section loaded with Ar upto 500-650 Torr depending on the desired reflected temperatures. After that ball valve is close in the driven section and then evacuate the sample section again with turbomolecular pump upto 10^{-6} Torr. Then we loaded 0.2 ml of liquid sample (measured using a micropipette). Before the sample has been loaded in the test section, the liquid sample is subjected to purification through a freeze-pump-thaw procedures so as to remove any dissolved volatiles and air. The liquid sample is then inserted into the sample chamber of shock tube using a sample holder (figure 2.4). After that the sample is diluted using Ar upto 500-650 Torr. To mix homogeneously, the diluted sample is then kept for 3 hours. At the same time driver section is also evacuated using a turbomolecular pump (Adixen, ATP 400) upto 10^{-5} torr. After that helium is filled rapidly in the driver section till the breakdown pressure of the aluminum diaphragm. Instantaneous bursting of the aluminum diaphragm forms a shock wave in the driver section with the velocity of 2 to 3 times to that of the sound wave in the medium ahead of it.

Figure 2.4: Sample loading adaptor. Left: assembled sample holder used to load sample into shock tube . Right: disassembled sample holder



Tek

Acq Complete M Pos: 1.980ms

CH2

Coupling
AC

BW Limit
Off
100MHz

Volts/Div
Fine

Probe
1X
Voltage

Invert
Off

CH1 48.0mV M 500µs CH2 ⁄ 32.0mV

CH1 vertical position −2.44 divs (−117mV)

Figure 2.5: A typical pressure trace recorded in by the oscilloscope showing the arrival of the primary and the reflected shock wave

The ratio of the shock wave velocity to the sound velocity in the medium ahead is defined as the Mach number, and is designated as M_s. The test gas molecules will be heated to temperature T_2 after the primary shock front crosses these molecules. When the primary shock wave crosses the first piezoelectric transducer, the resistance of the piezoelectric surface changes resulting in the change of output of voltage, which is further amplified and fed into the osciloscope. This primary shock triggers the osciloscope. Using this distance between two piezoelectric transducer and time, the velocity and hence, the Mach number of the shock wave (M_s) can be estimated. The primary shock wave travels and gets reflected at the end flange. The reflected shock wave will be traveling in the driven section back, where the test gas is heated previously by the primary shock wave. When this reflected shock travels through the test gas molecules, they will further be heated to reflected shock temperature (T_5). Similarly, there will be pressure jumps across the primary (P_2) and the reflected shock (P_5) wave fronts. Tektronix oscilloscope has been used for recording these pressure jumps across the primary and reflected shock fronts. A typical pressure trace has been displayed in figure 2.5. Details of growth of shock wave[1], selection of gases[1], effect of initial pressure on the experimental conditions[3], and importance of dump tank have been described previously elsewhere[4,5].

2.1.4 Calibration of Shock Tube

Theoretically all the physical properties behind the reflected shock waves can be directly calculated using conventional Rankine–Hugoniot relations for the normal shock waves which describe the change in P and T across the shock front[1,6]. Generally, the temperature behind the shock wave is calculated from the following shock wave relations:

$$\frac{P_2}{P_1} = \frac{2\gamma M^2 - (\gamma - 1)}{\gamma - 1} \tag{2.1}$$

$$\frac{T_2}{T_1} = \frac{[2\gamma M^2 - (\gamma - 1)][(\gamma - 1)M^2 + 2]}{(\gamma - 1)^2 M^2} \tag{2.2}$$

$$\frac{T_5}{T_1} = \frac{[2(\gamma - 1)M^2 + (3\gamma - 1)][(3\gamma - 1)M^2 - 2(\gamma - 1)]}{(\gamma + 1)^2 M^2} \tag{2.3}$$

where M = mack number, γ = heat capacity ratio.

However temperature calculations using these ideal shock relations are not accurate due to several reasons including boundary layer problems, real gas effects, exo/endothermicity of the chemical reactions, etc. So, the temperature experienced by the test gas in the reaction zone differs from what has been estimated using above relations. For kinetics study, temperature is the important parameter which needs to be known accurately as rate constants have an exponential dependence on temperature. One approach to overcome these problems is to calibrate the temperature in terms of the kinetics of a known reaction[2] and the approach is known as chemical thermometry. Details about chemical thermometry has bern mentioned elsewhere[7] and only a brief about it has been discussed here. In the case of "internal" chemical thermometry, reflected shock temperature is determined by following the progression of a standard reaction with a known rate constant, which is investigated together with the reaction of interest. Whereas in the case of "external" chemical thermometry, experiments with the standard are done independently, at various temperatures and a calibration curve is drawn between the measured temperatures and the calculated one based on the previously mentioned equations. The expression used for calculating temperature behind reflected shock wave involving use of internal standard is the following:

$$T = (-E_a/R)/[\ln(-\frac{1}{A \times t}\ln(1-\chi))] \tag{2.4}$$

where t is the reaction dwell time, E_a is the activation energy and A is the pre-exponential factor for decomposition of the internal standard, and χ is the extend of the standard reaction.

$$\chi = [product]_t/[product]_t + [internalstandard]_t$$

where $[product]_t$ is product concentration of internal standard at time 't', and $[internalstandard]_t$ is the unreacted concentration of internal standard at time "t".

However, with internal chemical thermometry approach, one must be careful to ensure that the internal standard does not interfere with the chemical reactions of the test molecule at all. To avoid those issues we have used a modified technique known as external chemical thermometry. The external chemical thermometry also use 2.4 for the calculation of temperature behind reflected shock wave. The obtained temperatures are then plotted against the reflected shock temperatures calculated by conventional Rankine-Hugoniot relations followed by least squares fitting of the resulting plot which is used to determine T_5 for all the experiments.

In our experiments we used two chemical thermometers. Ethyl chloride has been used for the calibration of temperature range of $950 - 1300$ K (as already reported by Singh et al.[7]) and 1,1,1-trifluroethane over the temperature range of $1300 - 1500$ K.

2.1.5 Shock tube calibration using 1,1,1-trifluroethane as external standard

The thermal decomposition of 1,1,1-trifluoethane (external standard) has been performed at varying P4/P1 conditions in the chemical shock tube with the objective of obtaining a calibrated reflected shock temperature over the temperature range of 1300-1500K. The pyrolysis of the standard sample has been studied for the reflected shock temperatures (T_5(Ms)) (calculated using shock Mach number) ranging from 1283 to 1584 K and P5 ranging from 10 to 25 atm while reaction time (dwell time) ranges from 1.31 to 1.54 ms. In the studied temperature range, the HF elimination channel has been found to be the only thermal decomposition pathway.

$$CH_3CF_3 \rightarrow CH_2CF_2 + HF$$

Both the reactant (1,1,1-trifluoethane) and product (1,1-difluoethene) have been identified and quantified using Agilent Gas Chromatograph (Model: 6890A) having Q-plot column installed in it. For the quantification purposes, the calibrations of 1,1,1-trifluroethane and 1,1-difluroethene in GC- Flame Ionisation detector (FID) have also been performed separately. A Chromatogram is shown in figure 2.6 identifying the species present in the post-shock reaction mixture.

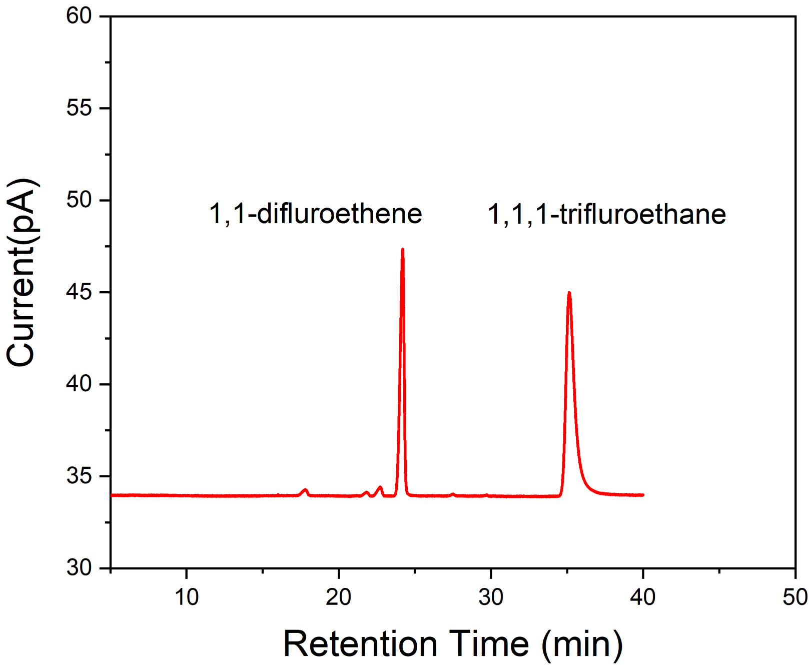


Figure 2.6: Chromatogram of a typical post shock mixture of 1,1,1-trifluoethane decomposition

The experimental temperature ($T_{5(kin)}$) for the reaction has been calculated by putting the experimental rate constant values in the Arrhenius expression reported for the same reaction by Akira et al.[8] for the temperature range of 1000-1600K.

$$k_{expt}(sec^{-1}) = 5.71 \times 10^{46}T^{-9.314}\exp[47073K/T]$$

Table 2.1: Summary of the experimental results of 1,1,1-trifluoethane pyrolysis for T_5 calibration

Sl. No.	Dwell time(ms)	T_5(Ms) (K)	T_5(kin) (K)	$[C_2H_3F_3]_t$ $/[C_2H_3F_3]_0$	$[C_2H_2F_2]_t$ $/[C_2H_2F_2]_0$
1	1.31	1283	1277	0.93300	0.06720
2	1.46	1294	1283	0.91400	0.08590
3	1.40	1318	1300	0.88400	0.11600
4	1.46	1344	1320	0.82500	0.17500
5	1.47	1371	1336	0.76700	0.22200
6	1.44	1384	1328	0.80000	0.19000
7	1.44	1396	1361	0.65900	0.32500
8	1.54	1459	1378	0.54200	0.42000
9	1.48	1497	1412	0.34100	0.60300
10	1.44	1498	1423	0.29100	0.65600
11	1.48	1546	1439	0.18900	0.66900
12	1.48	1561	1441	0.17700	0.64100
13	1.44	1584	1465	0.08480	0.73700

The experimental $T_{5(kin)}$ are plotted against $T_{5(Ms)}$ obtained with the reflected shock mach number. The least square fitting of this data has been performed (Figure 2.7) to determine experimental T5 which can be used as the actual experimental temperature for the future experiments that will be performed within the specified temperature range.The correlation between $T_{5(kin)}$ and $T_{5(Ms)}$ within the experimental $T_{5(Ms)}$ range of $1283 - 1584$ K is found to be:

$$T_{5(kin)} = 0.6135 \times T_{5(Ms)} + 491.7268 (R^2 = 0.99)$$

The uncertainty in the calibrated temperature is estimated up to 25K. It can be clearly seen from the above plot that the calculated temperature, $T_{5(Ms)}$ overestimates the actual temperature, $T_{5(kin)}$, and the difference increases with increasing temperature. The reflected shock temperatures calculated using Mach number, $T_{5(Ms)}$ and that obtained from the measurement of extent of 1,1,1-trifluroethane

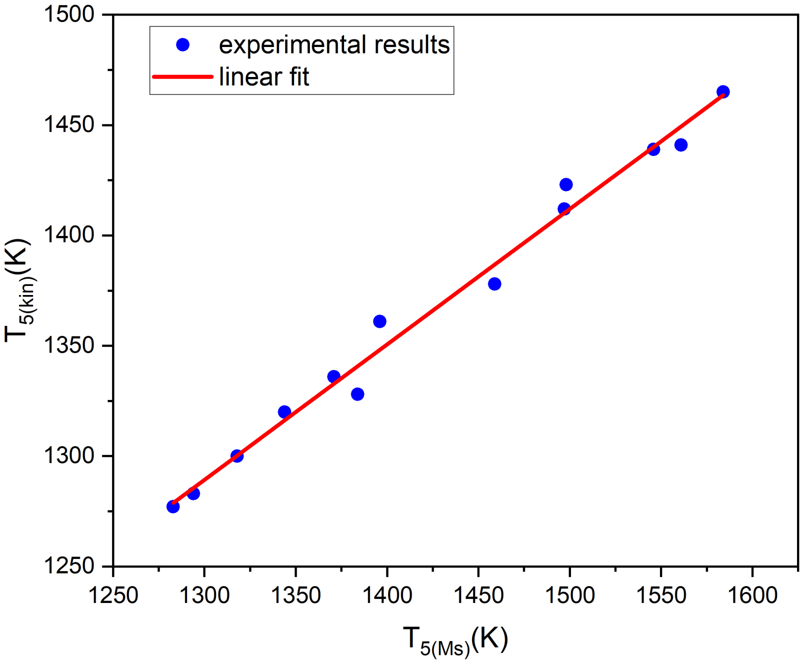


Figure 2.7: Plot of experimental $T_{5(kin)}$ Vs theoretical $T_{5(Ms)}$ showing their correlation within the experimental temperature range $1277 - 1465$ K.

decomposition, $T_{5(kin)}$ differed by $0.47 - 7.51\%$ in the calibrated temperature range. The higher discrepancy (between the two temperatures) observed at the higher temperatures is obviously expected as the T_5 calculation using conventional Rankine-Hugoniot relations does not account for the non-idealities in the reflected shock wave.

2.1.6 Analysis of Post-shock Mixture

The accurate analysis of the post-shock mixtures determines the accuracy of the experimental results. So, the concentrations of all the species involved in the reaction has to be measured accurately in order to obtain reliable kinetic parameters in addition to the accurate measurement of the reaction time and temperature. In all our experiments the reactant and products molecules have been analysed using Gas Chromatography (GC) technique. GC is the best quantitative technique for the analysis of gas phase samples.

2.1.6.1 Gas Chromatography

Chromatography is a broad technique where separation of the mixture components is achieved by their distribution between a fluid mobile and a stationary phase. In gas chromatography the mobile phase is a gas and the stationary phase is liquid adsorbed on a solid support. The gas chromatography workes on the basis of selective adsorption of different components in a mixture as they are carried by the mobile phase (gas) through a column packed with finely ground adsorbent materials. When the mixture components move through the column, successive adsorptions and desorptions occurs. Those components which are adsorbed least strongly will move most rapidly and with time the mixture components get seperated from each others. Hence the separation of compounds in the mixture are based on the successive adsorptions and desorptions processes. As the degree of adsorption and desorption depends on the temperature, for better separation it is essential to keep the column at an optimum temperature. Gas chromatography consist of three main sections: injector, oven and detector. Mixture samples has been injected into the GC through injector, which is generally kept at a temperature where the chemical under consideration is completely vaporized. Oven houses the column through which sample mixture is passed and separated. The exit side of the column will be connected to a detector which quantitatively/qualitatively identify the components of the mixture sample. The schematic diagram of the basic gas chromatograph set-up

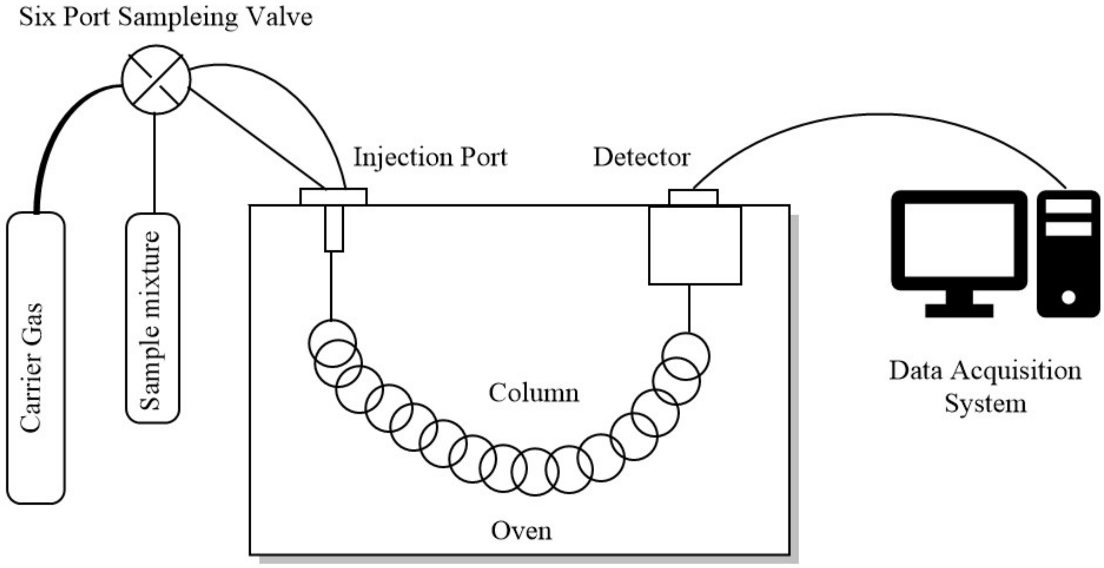


Figure 2.8: Schematic diagram of the basic GC set up.

is shown in the figure 2.8. In our experiment, we used two different Gas-

Chromatography. One Gas-Chromatography is with dual Flame Ionization Detectors(FIDs) set-up i.e. GC-FID/FID (Agilent 7890B) and the other one is with Mass Spectrometer (GC-MS) detector (Agilent 7890A). These two GC have been used to quantify and identify products in the post shock mixtures.

2.1.6.2 Flame Ionization Detector (FID)

In the FID, there are two electrodes, which are maintained at a constant potential difference (about 300V). In between the electrodes oxygen and hydrogen are lit to give the flame. Arrangements are made for hydrogen and oxygen gas to flow through it. When the compound is eluted out of the column, it will be ionized in the flame between the electrodes. The ions are captured by the electrodes, whereby causing a sudden change in the potential difference between the electrodes because of the additional current due to the ions. The magnitude of the potential difference between the electrodes due to the ions depends on the concentration of the compound that is eluted. The change in the output current is directly proportional to the concentration of component eluting at detector end of the column as well as the sensitivity of the detector to it.

2.1.6.3 Mass Spectrometer (MS)

The MS mainly consists of ionization chamber, mass filter, detector, heaters and radiator and detects the molecule using mass/charge ratio. Ion source ionizes the molecules exiting out of the column. The ionized molecules are then made to move through quadrupole mass filter. Filtered mass is then focused on to the detector generating an electrical signal proportional to number of ions. The heaters and radiators maintain the temperature in the detector.

2.1.6.4 Column

In the Gas-Chromatography with dual FIDs set-up (GC-FID/FID), we have used two columns. The quantification of light hydrocarbons ($<C_5$) has been achieved using GC-FID with chromatographic HP-PlotQ columns while the post shock high mass hydrocarbons (C_5 and beyond) with the other FID in the dual-FID set-up which is connected to HP-5 column. In the Gas-Chromatography with mass spectrometer detector (GC-MS), we have used DB-1 column to identify hydrocarbons with m/z >42.

2.1.7 Calibration of GC-FID/FID

The sensitivity of any detector is, in general, different for different compound. In the present work, determination of sensitivity factor has been carried out for all the compounds towards the flame ionization detector (FID). The area under curve of a chromatogram representing a particular compound in a mixture is directly proportional to the concentration of the compound and sensitivity of the detector to the compound. To obtain the concentration of a compound from area under the curve, one needs to know the sensitivity of detector to the given compound. Usually it depends on number of C-C and C-H bonds present in the molecule. Sample cells of volume 2 liters, has been used to prepare samples required for sensitivity analysis of FID. The cells are evacuated and loaded with argon and blank runs have been taken to ensure that it is free of contamination. The cell is again evacuated and a known amount of sample is then loaded into the sample cell. The sample is then diluted with a known amount of Argon and allowed to mix for 3 hours and then finally injected into the GC-FID/FID. The area under curve of chromatogram is then noted. The sample cell is evacuated to half pressure and again diluted with Argon. The area under the curve is again noted and the procedure is repeated until the area under the curve nearly becomes zero.

Table 2.2: Summary of sensitivity factor of FID-1 to the molecules used in present work. * estimated sensitivity factor.

Molecule	Sensitivity factor (pA^2)
Methane	3.46821E+5
Ethene	4.11997E+5
Acetylene	5.22234E+5
Propene	5.28287E+5
Propane	5.07297E+5
Propyne	6.51541E+5
1,3-butadiene	5.44451E+5
Vinyl acetylene	6.00301E+5
Butene	4.97055E+5
Ethane	2.73847E+5
1,1,1-trifluroethane	3.87820E+5
1,1-difluroethene	4.21460E+5
1,3-butadiyne*	5.91847E+5
butyne*	5.62231E+5

A plot of area under the curve vs mole fraction of a particular compound is linear fitted to obtain the sensitivity of the detector to that compound. This is used to convert the area profile into concentration profile. Figures 2.20 to 2.22

shows calibration curves for molecules which are needed in the present work. The sensitivity factor of two detectors to different molecules are tabulated in 2.2 and 2.3. In our experiment we have assumed sensitivity factor of isomers are same. Few moleculs are not available in the market in a stable form to do calibration. For those molecules we have estimated the sensitivity factor which are marked on the table with '*' mark. For the calibration, the estimated uncertainty is upto 5 %.

Table 2.3: Summary of sensitivity factor of FID-2 to the molecules used in present work. * estimated sensitivity factor.

Molecule	Sensitivity factor (pA^2)
Benzene	4.93798E+5
Toluene	4.57491E+5
Styrene	3.99925E+5
1,3,5-trimethylcyclohexane	2.04602E+5
Cyclopentene	6.36794E+5
Cyclopentane	6.08735E+5
1,4-pentadiene	6.44787E+5
Pentene	6.16861E+5
3-methyl-1,4-pentadiene	6.25369E+5
1,3-cyclohexadiene	6,55587E+5
Cyclohexane	7.83032E+5
Hexane	5.55120E+5
1,3-dimethylcyclohexane	3.63825E+5
Cyclohexene	3.03995E+5
Ethylidenecyclohexene	2.12844E+5
Isopropylcyclohexane	1.51420E+5
Cyclopentadiene*	6.64853E+5
2-methyl-1,3-butadiene*	5.25033E+5
5-methyl-1,3-cyclopentadiene*	6.45435E+5

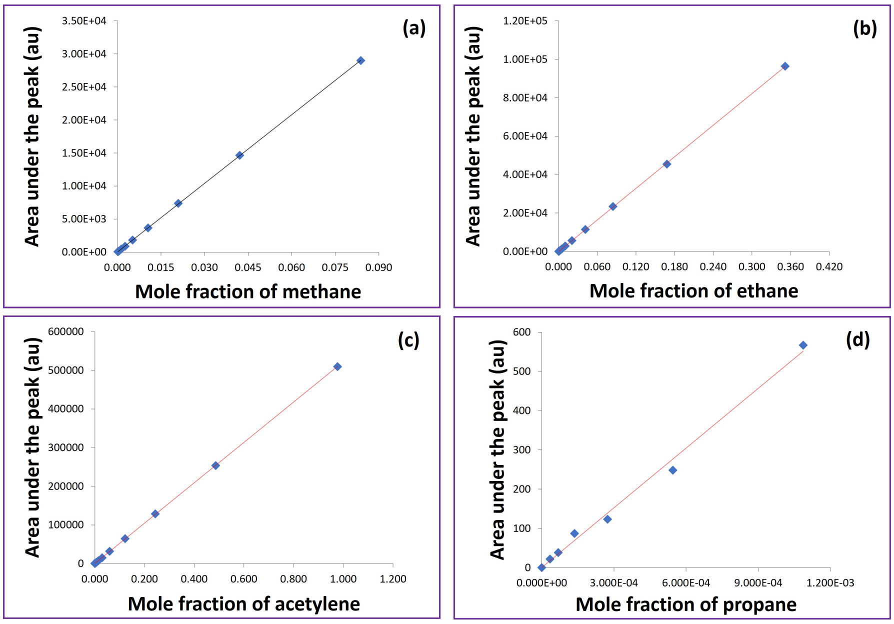


Figure 2.9: Calibration plot of (a)methane, (b)ethane, (c)acetylene and (d)propane.

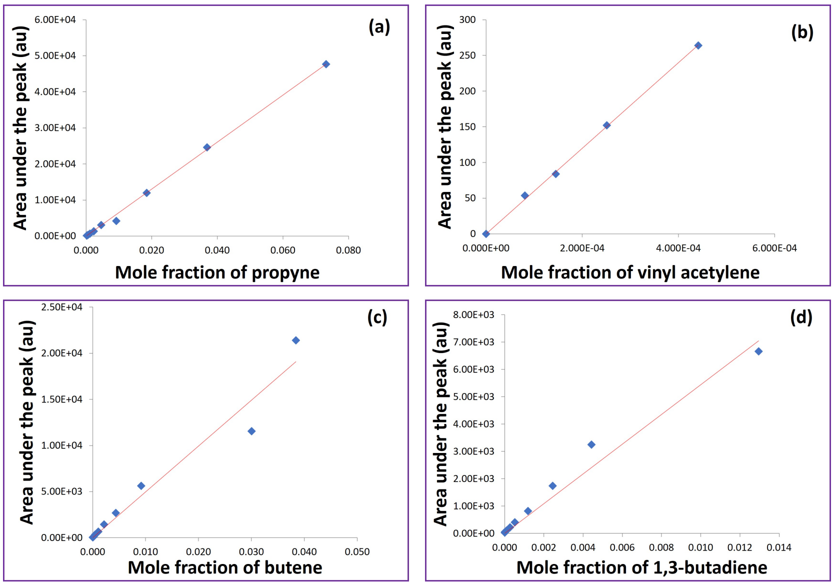


Figure 2.10: Calibration plot of (a)propyne, (b)vinyl acetylene, (c)butene and (d)1,3-butadiene.

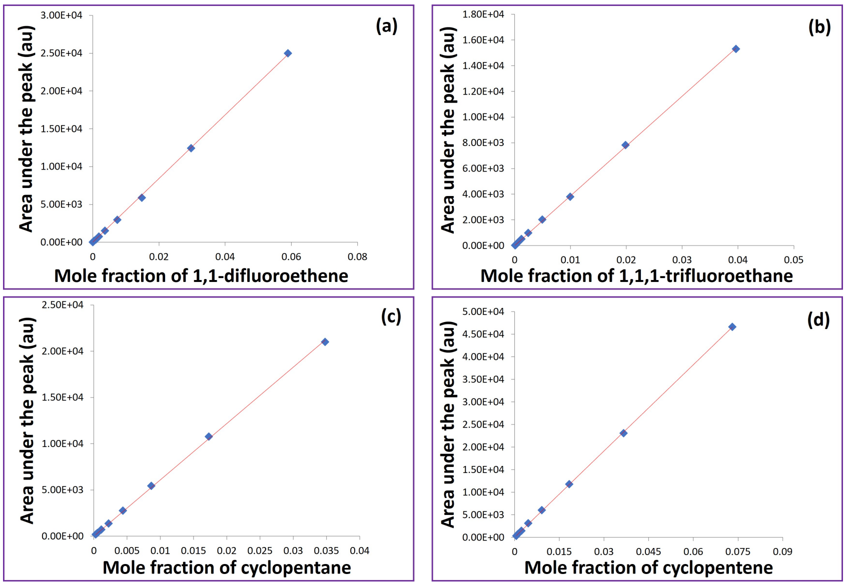


Figure 2.11: Calibration plot of (a)1,1-difluoroethene, (b)1,1,1-trifluoroethane, (c)cyclopentane and (d)cyclopentene.

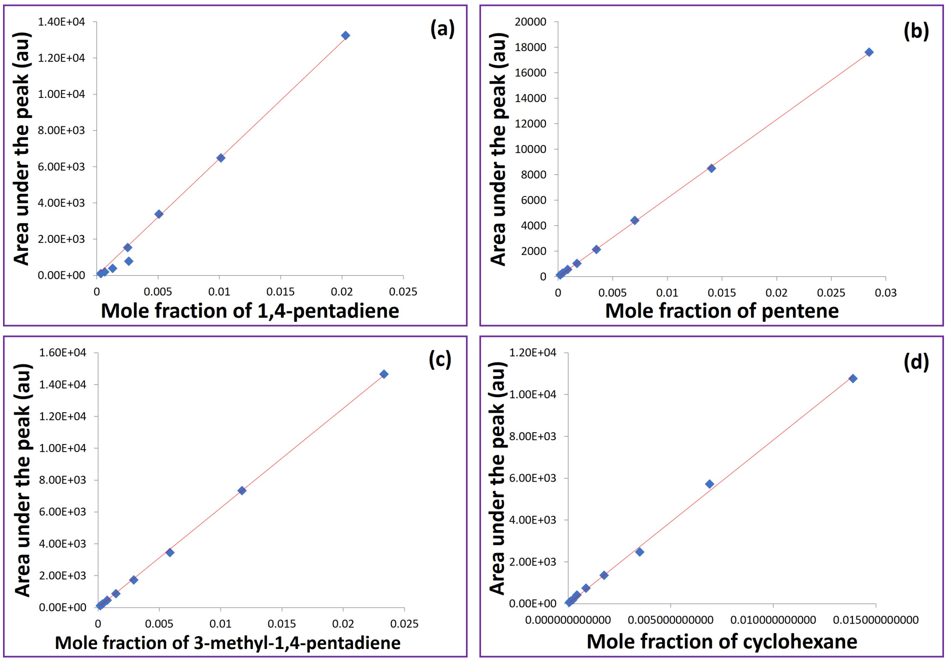


Figure 2.12: Calibration plot of (a)1,4-pentadiene, (b)pentene, (c)3-methyl-1,4-pentadiene and (d)cyclohexane.

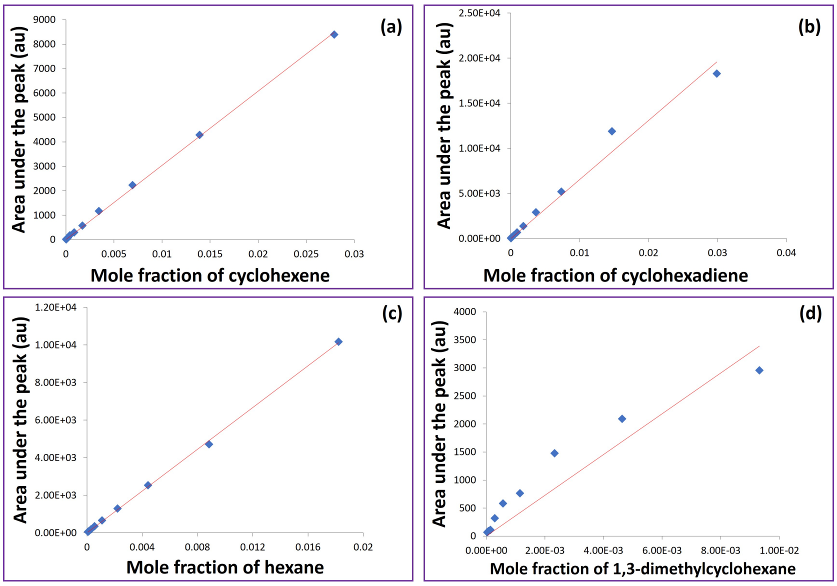


Figure 2.13: Calibration plot of (a)cyclohexene, (b)cyclohexadiene, (c)hexane and (d)1,3-dimethylcyclohexane.

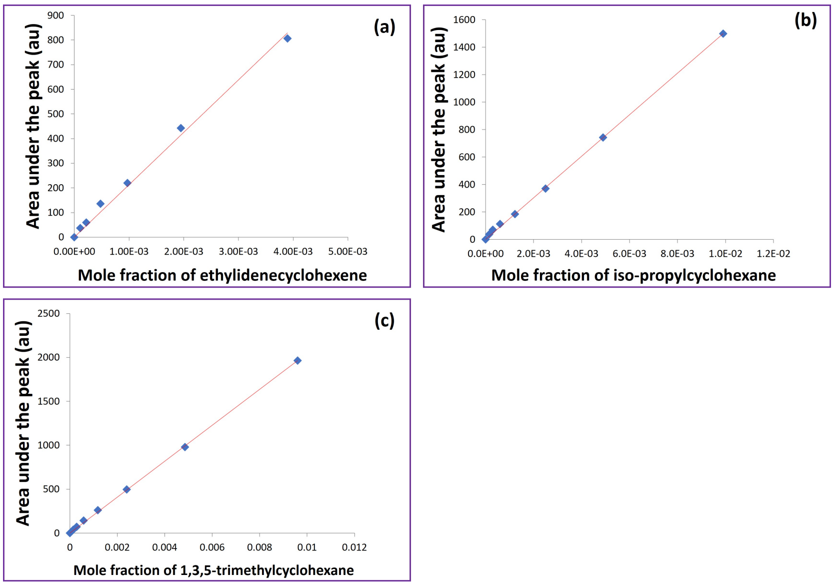


Figure 2.14: Calibration plot of (a)ethylidenecyclohexene, (b)iso-propylcyclohexane, and (c)1,3,5-trimethylcyclohexane.

2.1.8 Materials and chemicals

The list of chemicals and equipment used in the experiments are given bellow:

Gases: Helium (99.999%), Argon (99.999%), Nitrogen (99.99 %), Oxygen (99.99 %). These gases are supplied by Bhoruka Industrial Gases, India and Chemix. Hydrogen gas is generated using hydrogen gas generator.

Chemicals: 1,3,5-trimethylcyclohexane, iso-propylcyclohexane

Equipment:. Needle and ball valves (Swagelok), oscilloscope (Tektronix), Turbopump (Edwards and adixen), GC-FID (Agilent Technologies), GC-MS (Agilent Technologies).

2.2 Computational Methods

Along with the experiments, in this thesis we also report results from complete theoretical and kinetic simulation studies of the decomposition of molecules under consideration. Ab-initio calculations are important to understand the potential energy surface (PES) involved in decomposition of molecules under consideration. After getting the PES, we did rate calculations using TST/VTST theory of all elementary reactions. Then using all the rate paremeters from our calculations and from literature we have built the kinetic model and simulated our experimental results using Chemkin. In this section we have discuss about all those methods we used in this thesis.

2.2.1 Geometry optimization and frequency calculation

2.2.1.1 Single-reference Method

In this thesis, we mainly used CBS-QB3 method[9], which is a compound method. The CBS-QB3 method involves a five-steps calculation:

a) geometry optimization and frequency calculation at B3LYP/6-311G(2d,d,p) level (zero point energy (ZEP) scale factor is 0.99);

b) single point energy calculation at B3LYP/6-311G(2d,d,p) level;

c) single point energy calculation at MP4SDQ/6-311G(2d,d,p) level;

d) single point energy calculation at MP2/6-311G(2d,d,p) level;

e) complete basis set extrapolation to correct the total energy.

IRC calculations were done with the same method to confirm that transition state connect with the reactant(s) and product(s).

MP2(full) method with 6-31G(d,p) basis set also used for few calculations.

All calculations were performed using Gaussian 9[10] and Gaussian 16[11] program.

2.2.1.2 Multi-reference Method

For the molecule having low lying excited state and unstable biradical intermediate, we used multireference methods as those possesses multireference characteristics. Geometry optimizations for those have been carried out using CASSCF[12], CASPT2[13] and MRCI[14] method. For the transition state associated with biradical, we used CASSCF method for geometry optimizations and frequency calculations. All multireference calculations were performed using Molpro 2018 program[15].

2.2.2 Enthalpy of formation calculation

The thermodynamic parameters for the new species have been calculated in this work. Their frequencies and standard entropies have been calculated at CBS-QB3 method[9]. Their standard enthalpies of formation have been calculated using atomization energy. The expression for computing the atomization energy of the hydrocarbon is the following:

$$\sum D_0(xCyH) = xE_0(C) + yE_0(H) - E_0(xCyH) \tag{2.5}$$

where $E_0(C)$ is the energy of carbon, $E_0(H)$ is the energy of hydrogen and $E_0(xCyH)$ is the energy of hydrocarbon.

The enthalpy of formation at 0K is calculated using the following expression:

$$\Delta H_0^f(xCyH, 0K) = x\Delta H_0^f(C, 0K) + y\Delta H_0^f(H, 0K) - \sum D_0(cCyH) \tag{2.6}$$

where $H_0^f(C, 0K)$ is the standard enthalpy of formation of elements C and $H_0^f(H, 0K)$ is the standard enthalpy of formation of elements H at 0K temperature in their standard state. The enthalpy of formation at 298 K is then calculated using the following expression:

$$\begin{aligned}\Delta H_0^f(xCyH, 298K) = \Delta H_0^f(xCyH, 0K) + (H_{xCyH}^0(298K) - H_{xCyH}^0(0K))\\ - [x(H_C^0(298K) - H_C^0(0K)) + y(H_H^0(298K) - H_H^0(0K))]\end{aligned} \tag{2.7}$$

where $(H_{xCyH}^0(298K) - H_{xCyH}^0(0K))$ is the difference of enthalpy at 298K and 0K temperature. The experimental value of standard enthalpy of formation of elements C, and H $(H_x^0(298K) - H_H^0(0K))$ have been repoeted by Curtiss et al.[16] and we have used those values.

2.2.3 Rate calculation

2.2.3.1 High-pressure limit rates

High-pressure limit rates of all elementary reactions associated with saddle point were calculated with **transition state theory (TST)**, i.e.,

Table 2.4: Experimental enthalpies of formation, $\Delta H_0^f(0K)$, of elements and $H_o(298K)$–$H_0(0K)$ is taken for elements in their standard states. Both the values are given in kcal/mol and taken from the reported by Curtiss et al.[16]

Element	$\Delta H_0^f(0K)$	$H_o(298K)$–$H_0(0K)$
H	51.63±0.01	1.01
C	169.98 ±0.1	0.25

$$k(T) = \sigma \frac{k_B T}{h} \frac{q_{\neq}}{Q_R} \exp(\frac{\Delta E_0}{RT}) \tag{2.8}$$

where σ is symmetry number, k_B is Boltzmann constant, h is Planck's constant, T is the temperature, Q_R is the total molar partition function (consisting of translation, vibration, rotation, and hindered rotation), $q_{\neq}$ is the partition function of activated complex, and ΔE_0 is the energy barrier.

Variational transition state theory (VTST) was used to calculate the rate for those reaction which does not associate with any saddle point (barrierless reaction) (e.g., C-C bond dissociation, C-H bond dissociation etc.). In VTST the rate was calculated by minimizing the rate as a function of reaction coordinate(s) and temperature(T):

$$k_{VTST} = min k_{TST}(s,T) \tag{2.9}$$

where, $k_{TST}(s,T)$ is the rate at each point along the reaction coordinate.

For reactant and transition state, vibration frequencies correspond to torsion about a single bond (e.g., internal rotation of methyl group, iso-propyl group etc.) and are treated as 1-D hindered internal rotor using a symmetric hindrance potential function. The potentials for each internal rotation for reactant was calculated by relax energy scan of the dihedral angle with 10-degrees interval. For the transition state, the potentials of hindered internal rotations closest to the reaction centers were also computed with the bond lengths at the critical geometries frozen, while the other hindered internal rotations employ the scan results for the corresponding reactant.

High-pressure limit calculations were performed using the thermo (for TST) and ktools (for VTST) package of multiwell program suite[17–19].

2.2.3.2 Pressure dependent rates

To incorporate pressure dependency in rate, we used Multiwell Master Equation Code. It calculates time-dependent concentration, yield and rate constant as a function of temperature and pressure for unimolecular reaction[17–19]. Here we take

Argon as a collider, Bi-exponential model as a collision model. It is very difficult to compute proper energy transfer parameters, most of the case they are usually obtained by fitting experimental rate constant data. Here two parameters are needed to know:

a) Lennard-Jones(LJ) parameters: We take LJ parameter from literature for respective molecules.

b) Estimating energy transfer parameter α in exponential down model: Most of the case parameter α in the exponential model (single component of the bi-exponential model) is in the range from 100 cm^{-1} to 1000 cm^{-1}. We took 250 cm^{-1} as α value which is also suggested by manuals.

2.2.4 Kinetic model building/Simulation

The simulation of the pyrolysis has been performed with the normal reflected shock code whereas the sensitivity analysis have been conducted using the close homogeneous batch reactor code in CHEMKIN software. The thermodynamic data are fitted using fitDat function of the CHEMKIN software.

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Chapter 3

Iso-propylcyclohexane pyrolysis at high pressure and temperature

3.1 Introduction

Iso-propylcyclohexane (C_9H_{18}) has the following properties: molar mass of 126.24 gm/mol, melting point of 184 K, boiling point of 428 K, and density of 0.8±0.1 gm/cm^3.

As we discuss in the section 1.4, most of the previous studies of cyclo-alkanes have focused on cyclohexane and methylcyclohexane. Various experimental studies are found in the literature regarding oxidation, pyrolysis, flame and ignition (table 1.9) of methylcyclohexane at different temperature and pressure regions. However, long-chain n-alkyl-cyclohexanes have not received as much attention. Previous experimental studies on other cyclo-alkanes (e.g. ethylcyclohexane, n-propylcyclohexane and n-butylcyclohexane) are relatively less (table 1.9). We note that most of these studies focused on oxidation and investigated the macroscopic properties (e.g., ignition delay time, laminar flame speeds, etc.). Experimental investigations on high-pressure pyrolysis with detailed speciation have not been reported as extensively. Such studies are important in understanding the unimolecular decomposition pathways and reaction mechanisms for forming aromatic products. Survey of theoretical investigations on cyclo-alkanes show a similar situation (table 1.9).

Previous studies on the kinetic model development for alkyl-cycloalkane reported in the literature used rate parameters from reactions of smaller species with some similarity. While this would help in getting some quick insight into the problem, one can never be certain about how accurate the results would be. Hence, detailed theoretical investigation of alkyl-cycloalkane is very important to build a kinetic model. The scarcity of experimental, theoretical, and kinetic modeling data on pyrolysis of alkyl-cyclohexane so far motivated us to take up this present theoretical study of thermal decomposition of alkyl-cyclohexane. Iso-propylcyclohexane is the simplest cyclohexane which has both branched alkane (iso-alkane) and cyclohexane structural character. When this work started, there was no experimental or theoretical study of iso-propylcyclohexane pyrolysis/oxidation in the literature. One study report on its pyrolysis has appeared recently[1](table 1.9). Their study involved using a flow reactor to perform the experiments at temperature range of 880-1340K and pressure of 0.4 and 1 atm. This study describes attempts on building a kinetic model of pyrolysis of iso-propylcyclohexane wherein they estimated the rate parameters involved in the model mainly from the available data in literature. Theoretical investigations on the reaction pathways have not been carried out. A detailed investigation on thermal decomposition of iso-propylcyclohexane would help in understanding the effect of side-chain isopropyl group on the initial decomposition pathways and aromatic formation. In this work, we report results from a detailed theoretical investigation of thermal decomposition of iso-propylcyclohexane (IPCH) using high level of quantum chemical calculation. TST/VTST calculations have been used to obtain reliable rate constants for all important elementary reactions associated with iso-propyl-cyclohexane pyrolysis. These results have been used for detailed kinetic simulation of product profiles at various temperatures for comparison with shock tube experimental results.

3.2 Computational Details, Experimental Details and Kinetic Model

3.2.1 Geometry optimization and frequency calculation

The initial ring-opening path of IPCH is associated with unstable biradical intermediate, and the decomposition path involve C-C bond lengthening during the bond dissociation (figure 3.3). To calculate the accurate energy barrier for these steps, one needs the multireference method as the biradical possesses multireference characteristics. Geometry optimizations and frequency calculation for biradicals have been carried out using CASSCF method with the basis set of 6-31+g(d,p). For reaction associated with biradical intermediate, active space of six electrons occupying six orbitals (i.e., CAS(6e,6o) have been considered. A minimum active space (i.e.,CAS(2e,2o) has been chosen for CH_3 and C_3H_7 loss reaction channels. Single-point energies have been corrected using the MRCI method with the same active space and basis set. The zero-point energy (ZPE) scaling factor for the CASSCF method is 0.93[2]. For all other types of reaction single reference method has been used. In this work, we were using CBS-QB3 method (section 2.2.1.1). IRC calculations were done with the same method to confirm that the transition state connects with the reactant(s) and product(s). All multireference calculations were performed using Molpro 2018 program while Gaussian 16 program was used for CBS-QB3 calculation.

3.2.2 Reaction rate calculation

We calculated high-pressure limit rate in this work which is described in details at section 2.2.3.1.

Kinetic parameters A and E_a to be used in chemical kinetic modeling, were obtained by fitting the calculated rate constant over the 800-2000 K temperature range to Arrhenius expression.

$$k(T) = A\exp(-E_a/RT)$$

As we are getting good fitting with temperature coefficient, n=0 in our considered temperature range, the temperature co-efficient is taken as zero. All the rate calculations were performed using the multiwell 2020 program.

3.2.3 Experimental Details

The high temperature thermal decomposition of IPCH in argon bath has been carried out in the single pulse chemical shock tube (CST-1) facility available in our lab the details of which is given in section 2.1.2. IPCH used in the experiment has been procured from from TCI (Tokyo Chemical Industry) and is of 99% purity (cas no.: 696-29-7). 0.2 ml IPCH has been consistently taken for each experiment using a micropipette (vapour pressure of Iso-propylcyclohexane is 4 Torr).

3.2.4 Kinetic Model

Detailed kinetic modelling for ethylcyclohexane pyrolysis and oxidation has been used as the base mechanism for the proposed IPCH kinetic model[3]. For the submechanism for IPCH pyrolysis, rate parameters have been taken from theoritical calculation. The present kinetic model includes 426 species and 1354 reactions. The thermodynamic parameters for the new species found in IPCH mechanism have been calculated in this work as thermodynamic data for many of the dehydrogenation intermediates from IPCH are not available. Their frequencies and standard entropies have been calculated at CBS-QB3 method. Their standard enthalpies of formation have been calculated using atomization energy (section 2.2.2).

The formulae, nomenclature, and structure of those species have all been given in the supporting information. The pyrolysis simulation has been performed with the normal reflected shock code whereas the sensitivity analysis have been conducted using the close homogeneous batch reactor code in CHEMKIN software.

3.3 Results and Discussion

The thermal decomposition of IPCH can be classified in six classes of reactions as given below:

i) Unimolecular decomposition and isomerization of IPCH
ii) H-abstraction reaction by H atom and CH_3 radical
iii) Dissociation of alkene and alkyl-cyclohexene
iv) Decomposition and isomerization of alkyl-cyclohexane radicals
v) Decomposition and isomerization of alkenyl radicals
vi) Stepwise dehydrogenation of cyclic intermediate

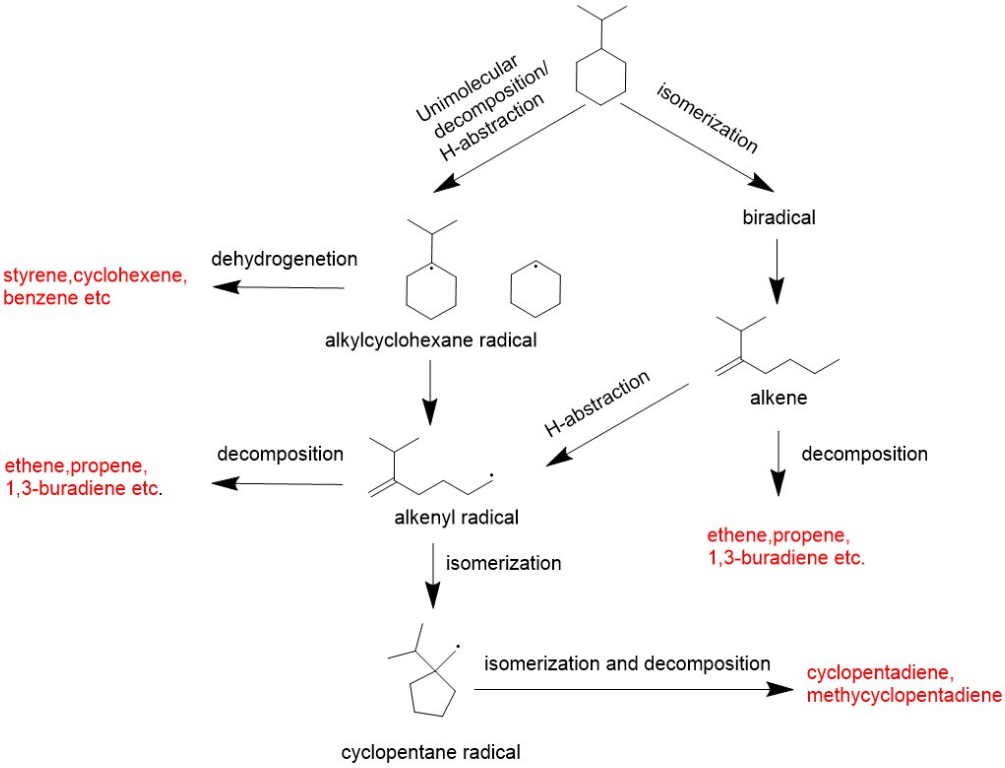

Figure 3.1: Global reaction scheme of IPCH thermal decomposition.

The global scheme of thermal decomposition of IPCH is shown in figure 3.1. The initial reaction involves the C-C bond dissociation from side-chain C_3H_7 group to form cyclohexane radical (by C_3H_7 group elimination) and secondary ethylcyclohexane radical (by CH_3 elimination) as well as ring opening of cyclohexane group to form seven types of alkenes through three different biradical intermediates. Then, chain reactions occur through the H-abstraction from six different C atoms within IPCH by H atom and CH_3 radical. The H-abstraction reactions results in formation of six types of alkyl-cyclohexane radicals which can either isomerize to form alkenyl radical or form cyclic intermediate/aromatic by sidewise dehydrogenation. Alkenes and alkenyl radicals decompose into small molecules and radicals (secondary reactions). In the following sections, we have first discussed the potential energy surface (PES) and analyzed the reaction mechanism of all kinds of reaction classes mentioned above. Thereafter, the rate parameters associated with each of the reactions involved have been discussed further. After that we will discuss experimental results and simulations.

3.3.1 Potential energy surface and analysis of reaction mechanism

We started our calculations with the lowest energy confirmer (i.e. chair confirmer with an iso-propyl group at equatorial position) based on the CBS-QB3 level.

3.3.1.1 Unimolecular decomposition and isomerization of IPCH

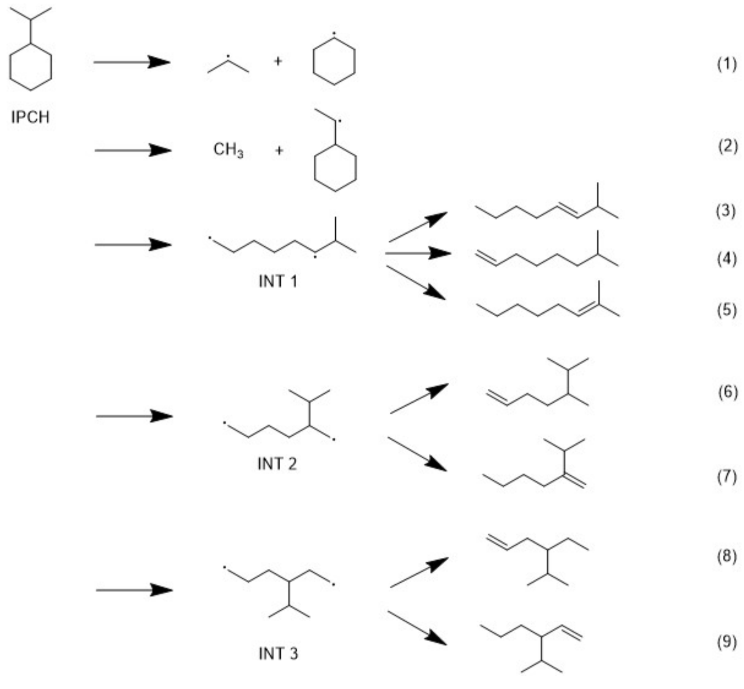

Figure 3.2: Decomposition and isomerization of IPCH.

In figure 3.2, we showed all the possible reaction channels of the initial decomposition and isomerization pathways of IPCH. In this process, two cyclohexyl radicals, three methyl-octene (through intermediate 1), and four isopropyl-hexene (through intermediate 2 and 3) are formed. We used the multireference method to calculate PES for these processes whereas for isomerization pathways (channel 3 to 9) we used six active space orbitals (three are bonding orbitals and three are antibonding orbitals). For the decomposition pathways (i.e., channel 1 and 2) we considered two active space orbitals associated with C-C bonding orbital and C-C antibonding orbital. Initial decomposition of IPCH has no saddle point along the reaction coordinate and the reverse reaction is barrier-less process.

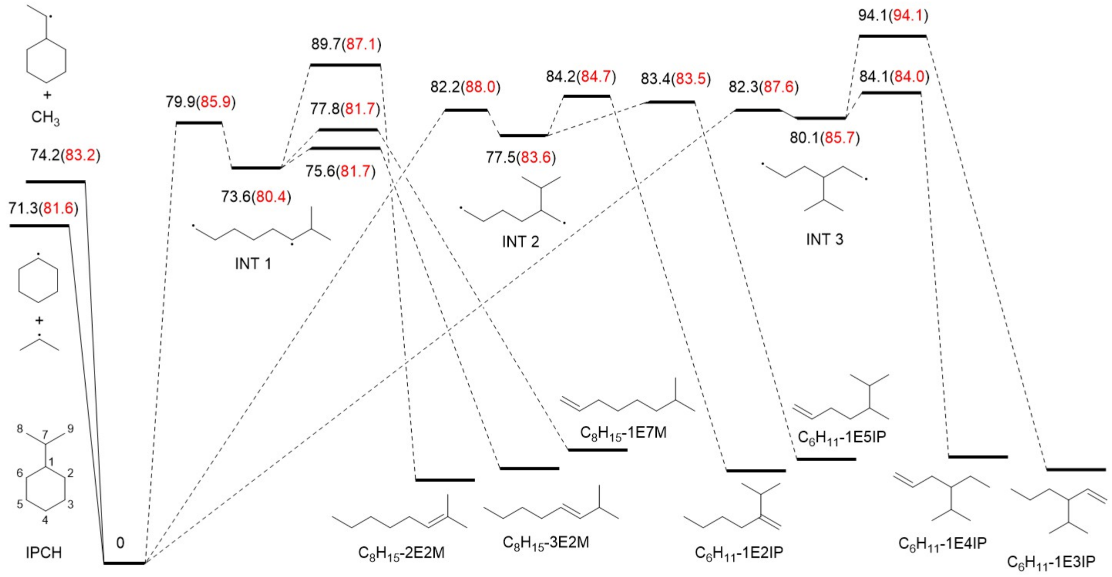

Figure 3.3: Potential energy surface for initial decomposition (side chain C1-C7 and C7-C9 bond dissociation) and ring opening isomerization (ring C1-C2, C2-C3, and C3-C4 bond dissociation) of IPCH. For initial decomposition, the methods were MRCI/6-31+g(d,p)//CAS(2,2)/ 6-31+g(d,p) (value in the bracket with red colure) and CAS(2,2)/ 6-31+g(d,p) (value with black colour). For isomerization, the methods were MRCI/6-31+g(d,p)//CAS(6,6)/ 6-31+g(d,p) (value in the bracket with red colure) and CAS(6,6)/ 6-31+g(d,p) (value with black colour). Energy unit: kcal/mol.

Figure 3.3 shows the calculated potential energy surface at MRCI//CAS(6,6)/6-31+g(d,p) (red colour) and CAS(6,6)/6-31+g(d,p) (black colour) level of theory for isomerization channel and that at MRCI//CAS(2,2)/6-31+g(d,p) (red colour) and CAS(2,2)/6-31+g(d,p) (black colour) level of theory for decomposition channel. The PES shows that the initial decomposition channel is more energetically favorable than the isomerization channel. The formation of cyclohexyl/iso-propyl radical channel (channel 1) is the most favored channel and has barrier 1.6 kcal/mol (MRCI method) less than that of CH_3 radical dissociation channel (channel 2). Isomerization happens with two steps. In the first step, the cyclohexane ring-opens with C-C bond dissociation and forming a biradical. In the next step, H-migration happens, and an alkene is formed. IPCH has three unique ring C-C bonds (C1-C2, C2-C3, and C3-C4), the dissociation of each (by ring-opening) can generate altogether three biradicals (INT-1, INT-2, and INT-3). The energy barrier to form INT-1 is the most favorable one among the three, whereas the energy barrier for the formation of INT-2 and INT-3 are similar. The energy difference between cyclohexyl/iso-propyl radical formation channel (channel 1) and INT1 formation channel is 4.3 kcal/mol, which is more than that of the similar reaction of methylcyclohexane dissociation (1 kcal/mol[2]). INT-1 is the most stable biradical followed by INT-2 and INT-3. This is expected due to an iso-propyl group's inductive effect (+I), which decreases with distance. H-migration from biradical to form alkene involves either a 6-member cyclic transition state (TS) or an 8-member cyclic TS and the former is energetically more favorable than later one. H-migration from INT-1 can form three methyl-octene. These are 2-methyl-oct-2-ene($C_8H_{15}-2E2M$), 2-methyl-oct-3-ene($C_8H_{15}-3E2M$), and 2-methyl-oct-2-ene($C_8H_{15}-1E7M$). Formation of $C_8H_{15}-2E2M$ happens via an 8-member cyclic TS. The energy barrier for this process is much higher than the energy barrier of the formation of $C_8H_{15}-1E7M$ and $C_8H_{15}-3E2M$, which happen via a 6-member cyclic TS. H-migration from INT-2 forms two alkenes, 2-iso-propyl-1-hexene ($C_6H_{11}-1E2IP$) and 5-iso-propyl-1-hexene ($C_6H_{11}-1E5IP$), and both formed via a 6-member cyclic TS, each involving similar energy barrier. Two alkenes, 4-iso-propyl-1-hexene ($C_6H_{11}-1E4IP$) and 3-iso-propyl-1-hexene $C_6H_{11}-1E3IP$) formed from H-migration from INT-3 via a 6-member cyclic TS have very different energy barrier (84.0 kcal/mol and 94.1 kcal/mol respectively, MRCI method). Due to the presence of iso-propyl group next (β position) to the H-migration site for $C_6H_{11}-1E3IP$ formation process, the correspondent cyclic TS experiences steric hindrance, making it unstable and thus has a high energy barrier. To understand the effect of the long side-chain group (iso-propyl group) in the initial decomposition and isomerization of alkyl-cyclohexane, in Table 3.1, we compare the energy barrier of our data with methylcyclohexane[2] data.

We can see that the initial decomposition that generate CH_3 radical has a similar energy barrier for both methylcyclohexane and iso-propylcyclohexane. But for iso-propylcyclohexane, another decomposition channel is available (dissociation to form iso-propyl group) which is more energetically favorable than the CH_3 elimination step. So, we can expect that iso-propylcyclohexane will dissociate faster than methylcyclohexane. Similarly, the cyclohexane ring-opening process

Table 3.1: Comparison of relative energy of initial decomposition and isomerization channel of methylcyclohexane and iso-propylcyclohexane. Energy unit: kcal/mol. Method: MRCI

	methylcyclohexane[2]	IPCH
C_3H_7 elimination channel	-	81.6
CH_3 elimination channel	84.0	83.2
TS of C1-C2 ring opening	85.0	85.9
TS of C2-C3 ring opening	89.0	88.0
TS of C3-C4 ring opening	89.0	87.6

has more energy barrier for methylcyclohexane than iso-propylcyclohexane except for C1-C2 bond breaking.

3.3.1.2 H-abstraction reaction by H atom and CH_3 radical

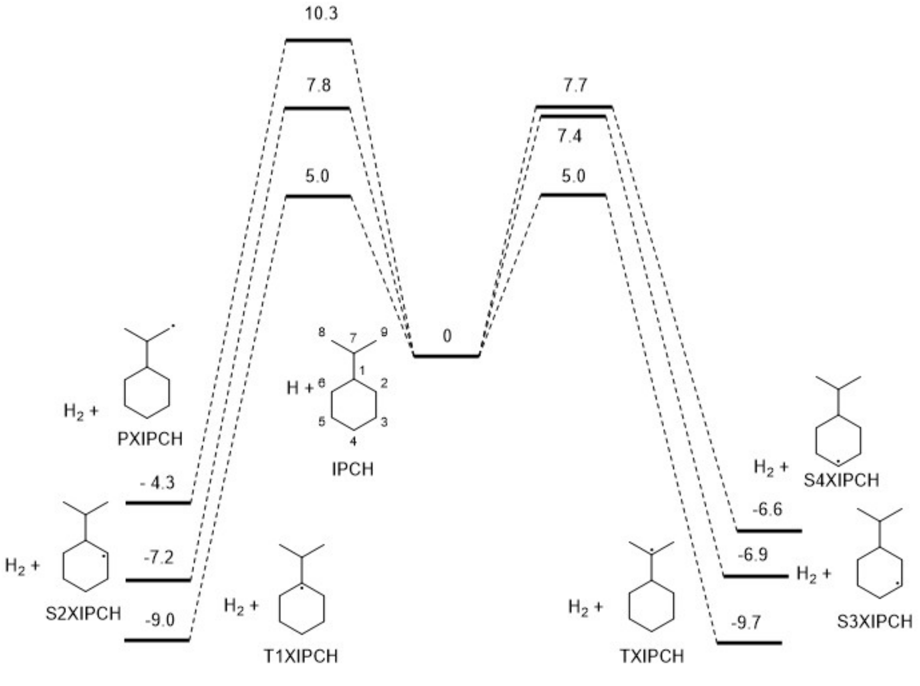

Figure 3.4: Potential energy surface for H-atom abstraction reactions of IPCH by H atom. Energy unit: kcal/mol

Except unimolecular decomposition and isomerization of IPCH, we have used CBS-QB3 level of theory for all other classes of reactions. As mentioned earlier,

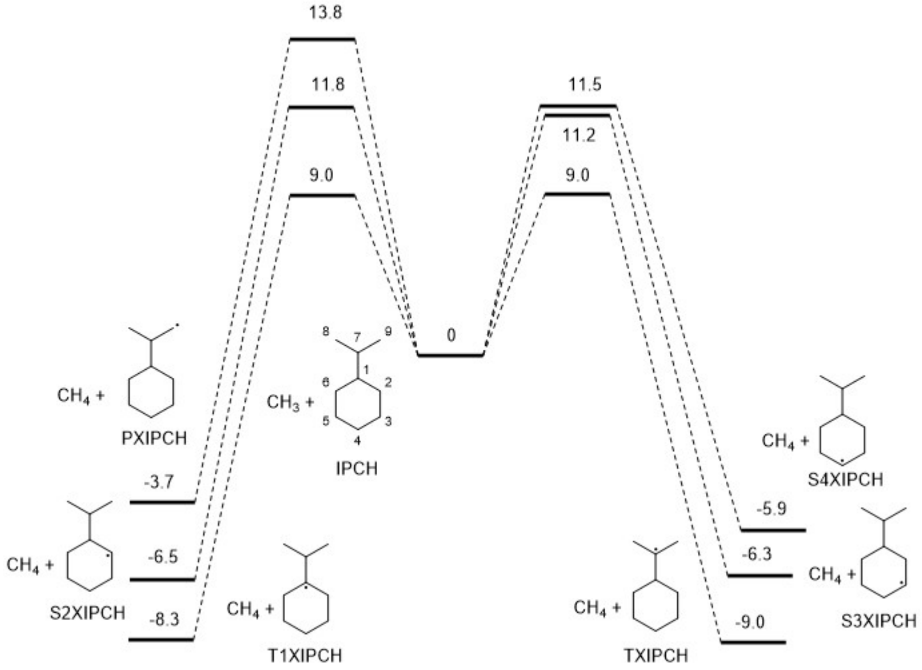

Figure 3.5: Potential energy surface for H-atom abstraction reactions of IPCH by CH_3 radical. Energy unit: kcal/mol

IPCH has six different C atoms, so six different alkyl-cyclohexyl radicals formed (through H- abstraction reaction by H atom/CH_3 radical). Figure 3.4 and Figure 3.5 show the potential energy surface for these types of reactions.

The energy barrier for H-abstraction by H atom is less compared to H-abstraction by CH_3 radical. The energy barrier for these type of reactions (abstractions) is

Table 3.2: Comparison of energy barrier of H-abstraction reaction by H atom between methyl-cyclohexane and IPCH. Energy unit: kcal/mol. Method: CBS-QB3.

	methylcyclohexane[4]	IPCH
Primary carbon H-abstraction	9.9	10.3
C1(H) abstraction	4.9	5.0
C2(H) abstraction	7.3	7.8
C3(H) abstraction	7.2	7.4
C4(H) abstraction	7.2	7.7

low. It follows the order: H-abstraction at the primary carbon>H-abstraction at the secondary carbon >H-abstraction at the tertiary carbon. In Table 3.2, we compare the energy barrier of the H-abstraction reaction of methylcyclohexane and IPCH by H atom.

3.3.1.3 Decomposition and isomerization of alkyl-cyclohexane radicals

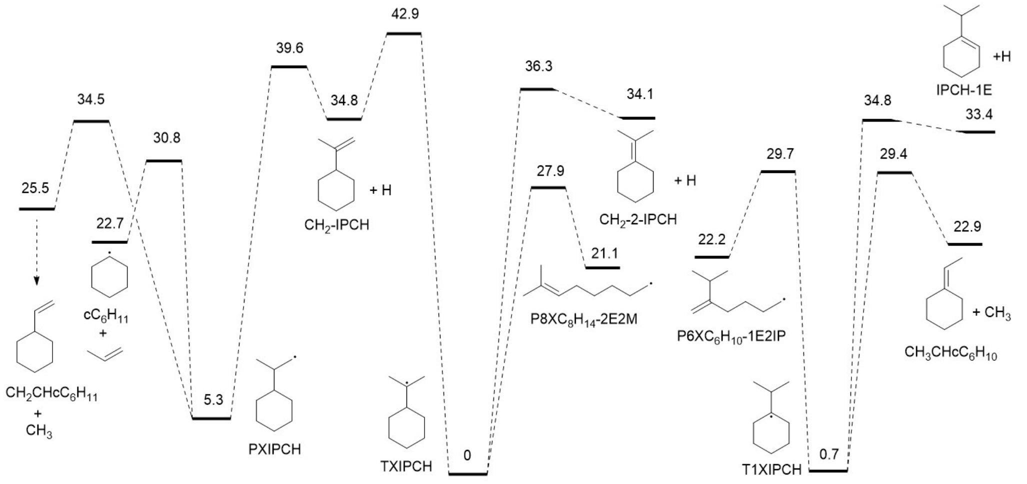

Figure 3.6: Potential energy surface for H-atom abstraction reactions of IPCH by CH_3 radical. Energy unit: kcal/mol

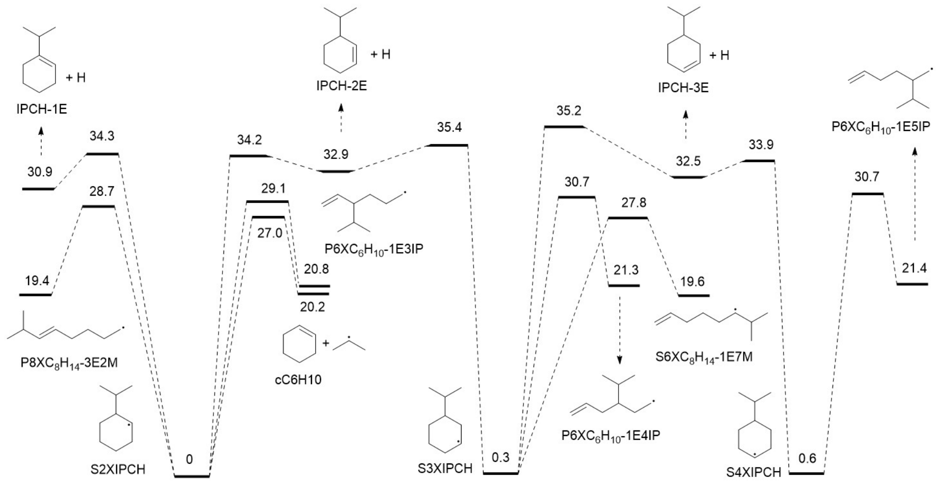

Figure 3.7: Potential energy surface for H-atom abstraction reactions of IPCH by CH_3 radical. Energy unit: kcal/mol

As shown in figure 3.4, the H-abstraction reaction leads to alkyl-cyclohexane radicals. Those radicals can further undergo either dissociation or isomerization.

Figure 3.6 and figure 3.7 show all these reactions of all alkyl-cyclohexane radicals. It can be seen that the dissociation occurs via either $\beta - C - C$ scission or $\beta - C - H$ scission and while isomerization takes place via $\beta - C - C$ scission to open the six-member ring. The energy barrier for the isomerization process is lower than those of other pathways for TXIPCH, S3XIPCH, and S4XIPCH, whereas dissociation via $\beta - C - C$ scission (i.e., CH_3 radical elimination, iC_3H_7 elimination) has lower barrier path for T1XIPCH and S2XIPCH. This characteristics for IPCH radical is different from methylcyclohexane radical and ethylcyclohexane radical. For methylcyclohexane radical, ring-opening isomerization process always has the lower barrier[4]. For ethylcyclohexane radical, the ring-opening isomerization process always has the lower barrier except for tertiary radical[3,5] (structurally similar with T1XIPCH). The energy barrier of dissociation via $\beta - C - H$ scission is higher among them (3-8 kcal/mol higher). The energetics corresponding to ring opening isomerization path for IPCH radical, methylcyclohexane radical and ethylcyclohexane radical have been compared in the table 3.3, shown below:

Table 3.3: Comparison between ring-opening isomerization of alkyl-cyclohexane radical. Energy unit: kcal/mol. MCH-methylcyclohexane; ECH-ethylcyclohexane.

Similar structure	C-C bond dissociation	MCH[4]	ECH[3,5]	IPCH
C1 carbon radical centre	One unique C-C bond	29.6	30.0	29.0
C2 carbon radical centre	adjacent to alkyl side-chain group	28.9	28.8	28.7
	far to alkyl side-chain group	29.5	29.1	29.1
C3 carbon radical centre	adjacent to alkyl side-chain group	28.7	28.5	27.5
	far to alkyl side-chain group	29.7	29.8	30.4
C4 carbon radical centre	One unique C-C bond	30.2	29.8	30.1

For ring-opening isomerization, C-C bond dissociation adjacent to iso-propyl group has a lower energy barrier than the other one for IPCH radical. There is a similar trend for MCH radical and ECH radical as well. Except for S4XIPCH (C4 carbon radical centre), energy barrier for ring-opening is less for IPCH radical than MCH radical and ECH radical, although the energy difference is within 1 kcal/mol. For IPCH radicals, among all the possible pathways $\beta - C - C$ scission of PXIPCH leads to propene(C_3H_6), and cyclohexane radical has the lowest energy barrier (25.5 kcal/mol). Table 3.4 shows the comparison of lowest energy path of methylcylcohexane radical, ethylcyclohexane radical and IPCH radical.

Table 3.4: Lowest energy pathway comparison between alkyl-cyclohexene radical. Energy unit: kcal/mol

	Bond dissociation	Energy barrier
MCH[4]	isomerization via $\beta - C - C$ scission	28.6
ECH[3,5]	dissociation via $\beta - C - C$ scission (CH_3 elimination)	28.0
IPCH	dissociation via $\beta - C - C$ scission (C_3H_6 elimination)	25.5

3.3.1.4 Dissociation of alkene and alkyl-cyclohexene

Alkenes which are formed by the initial isomerization process of IPCH can further undergo decomposition. In this work, we have considered both H-abstraction and C-C dissociation reactions. Liu et al.[6] studied C4-C6 alkenes theoretically and showed that allylic H-abstraction is the most energetically favourable. Hence,

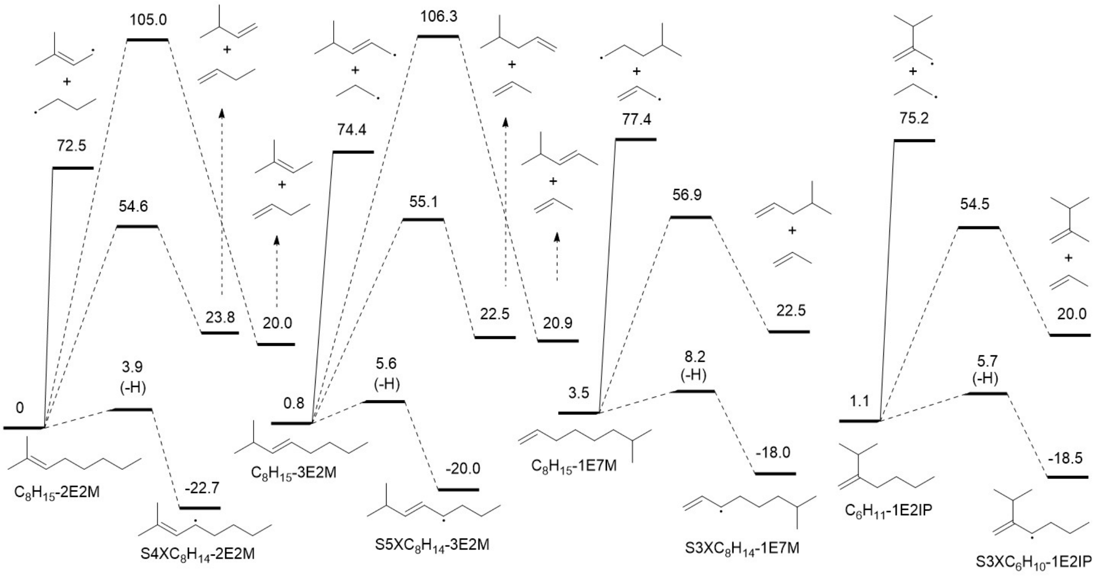

Figure 3.8: H-abstraction and decomposition reactions of $C_8H_{15}-2E2M$, $C_8H_{15}-3E2M$, $C_8H_{15}-1E7M$, and $C_6H_{11}-1E2IP$. (-H) indicates H-abstraction reaction by H atom. The solid line indicates reaction without saddle point. Energy unit: kcal/mol.

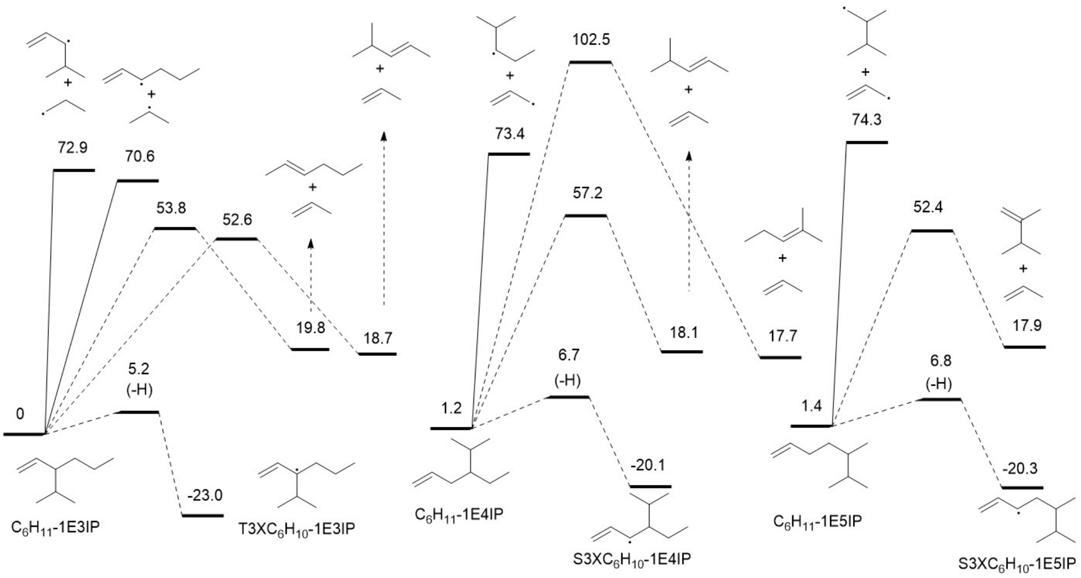

Figure 3.9: H-abstraction and decomposition reactions of $C_6H_{11}-1E3IP$, $C_6H_{11}-1E4IP$, and $C_6H_{11}-1E5IP$. (-H) indicates H-abstraction reaction by H atom. The solid line indicates reaction without saddle point. Energy unit: kcal/mol.

we have considered only the allylic H-abstraction reactions in the present study. Also,Wang's[7] theoretical study also showed that the allylic C-C bond has the lowest dissociation energy. Hence, we have considered only the allylic C-C bond dissociation in this work. Figure 3.8 and figure 3.9 show the PES of all the alkenes.

There are two types of C-C bond dissociation reaction:

a) simple bond dissociation reaction (which does not have any saddle point and is barrier-less reaction),

b) C-C bond dissociation followed by H-migration.

The C-C bond dissociation followed by H-migration through six-member ring cyclic TS has a significantly less energy barrier than that of H-migration through noncyclic TS. H-abstraction from $C_8H_{15}-2E2M$ is associated with the least energy barrier. Simple C-C bond dissociation of C6H11-1E3IP has the lowest energy barrier amongst all. The energy barrier for C-C dissociation followed by H-migration (through six-member ring cyclic TS) is lowest for $C_6H_{11}-1E5IP$. Alkylcyclohexene is formed from the elimination reaction of alkylcyclohexane radical. For IPCH-1E, IPCH-2E, and IPCH-3E, we have considered reverse Diels-Alder reaction as a dissociation channel (Figure x and Figure x). IPCH-2E has the lowest energy barrier for reverse Diels-Alder reaction These alkyl-cyclohexene can also form cyclic intermediate by stepwise dehydrogenation, which will be discussed later.

3.3.1.5 Decomposition and isomerization of alkenyl radicals

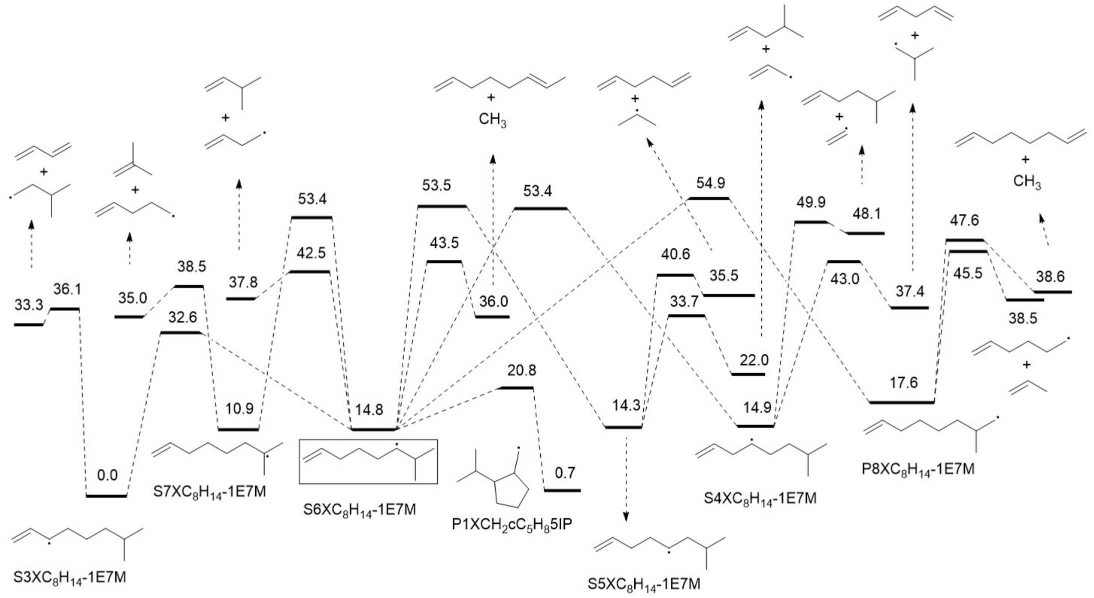

Figure 3.10: PES for decomposition reaction of $S6XC_8H_{14}-1E7M$. Energy unit: kcal/mol.

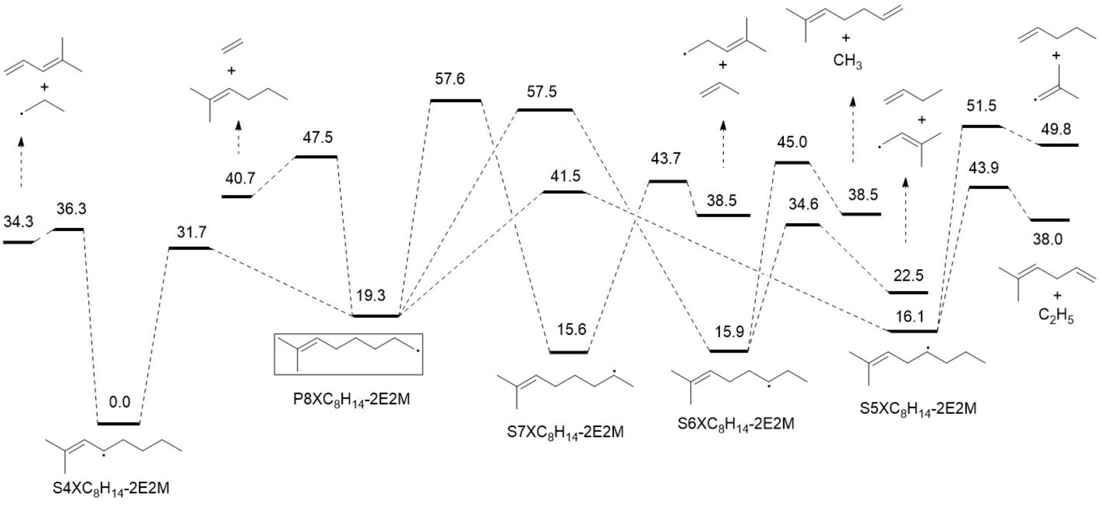

Figure 3.11: PES for decomposition reaction of $P8XC_8H_{14}-2E2M$. Energy unit: kcal/mol.

Different alkenyl radicals are formed by isomerization of alkyl-cyclohexane radicals and H-abstraction reaction of alkene. Here, we will discuss all the possible

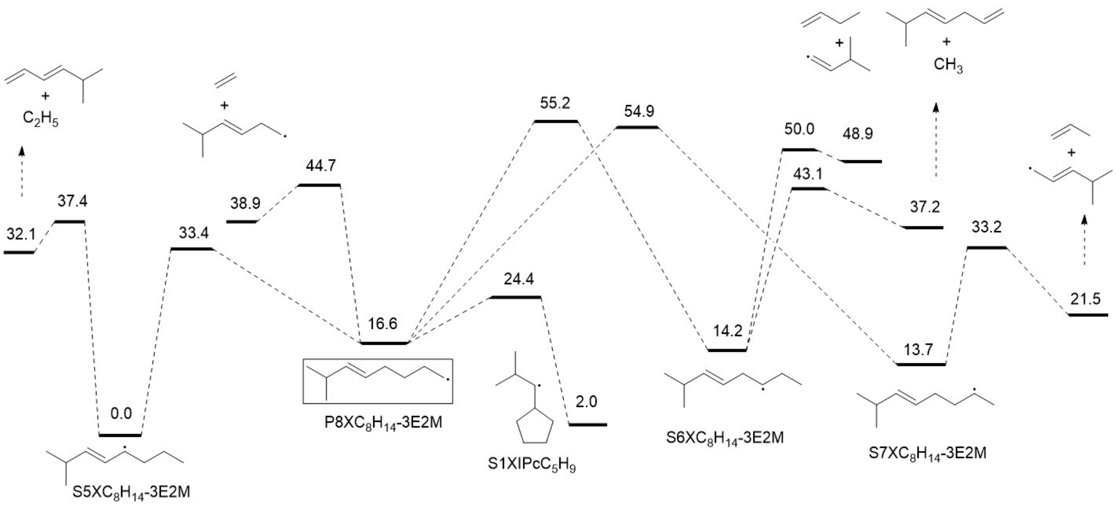

Figure 3.12: PES for decomposition reaction of $P8XC_8H_{14}-3E2M$. Energy unit: kcal/mol.

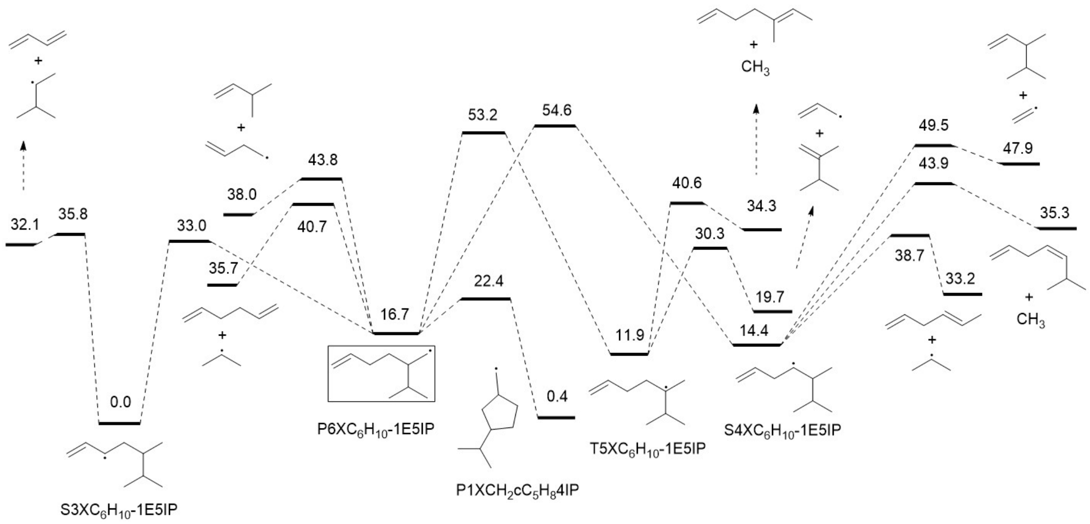

Figure 3.13: PES for decomposition reaction of $P6XC_6H_{10}-1E5IP$. Energy unit: kcal/mol.

pathways of decomposition of the alkenyl radical. Alkenyl radical can undergo either $\beta - C - C$ scission to form small hydrocarbon, or it can isomerize to form cyclopentane intermediate. It can also isomerize to other alkenyl radicals by intramolecular H-migration.

We can see from all PES (figure 3.10,3.11,3.12, 3.13, 3.14,3.15, and 3.16)

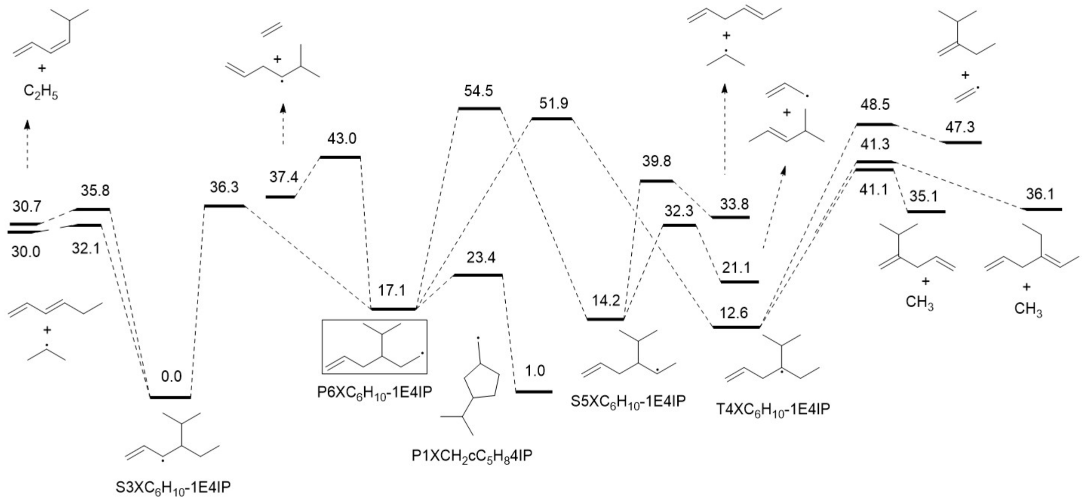

Figure 3.14: PES for decomposition reaction of $P6XC_6H_{10}-1E4IP$. Energy unit: kcal/mol.

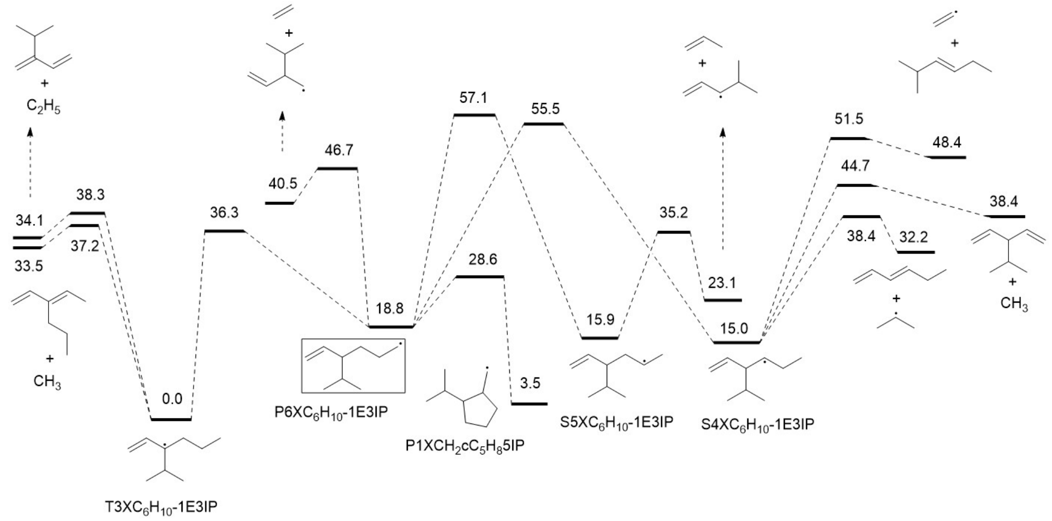

Figure 3.15: PES for decomposition reaction of $P6XC_6H_{10}-1E3IP$. Energy unit: kcal/mol.

that isomerization to cyclopentene radical is the lowest energy pathways (except P8XC8H14-2E2M where cyclopentane radical formation is not possible). For isomerization process by intramolecular H-migration; 1,5-H shift (only for $P8XC_8H_{14}-2E2M$) and 1,4-H shift (for all other alkenyl-radical) have lower energy barriers as these processes are associated with six-member cyclic TS (for 1,5-H shift) and five-member cyclic TS (for 1,5-H shift) respectively. $\beta-C-C$ scission of all the

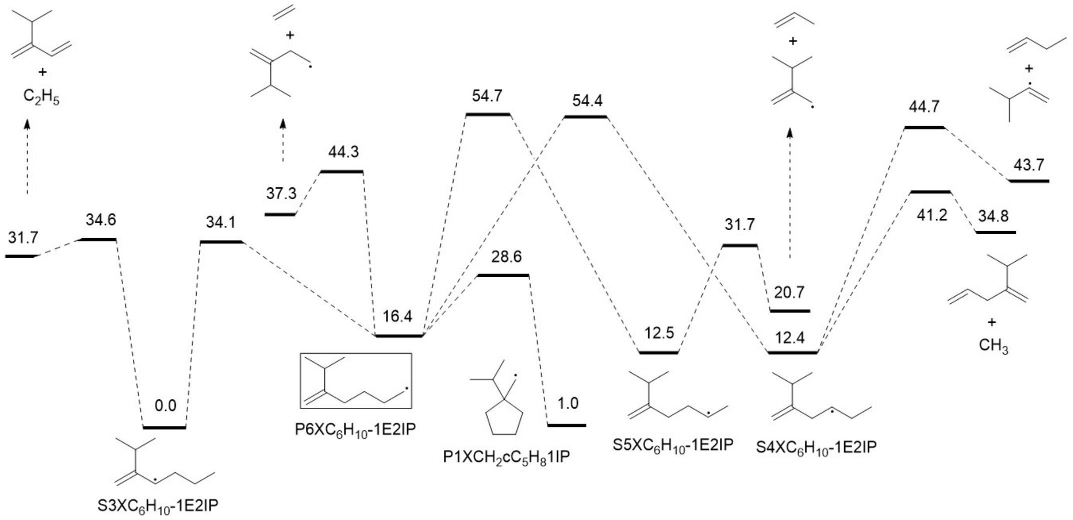

Figure 3.16: PES for decomposition reaction of $P6XC_6H_{10}-1E2IP$. Energy unit: kcal/mol.

alkenyl radicals leads to several small hydrocarbons which include diene (butadiene, methylpentadiene, pentadiene, hexadiene etc.), alkene (ethylene, propene, butene ect.), alkyl-radical (CH_3, C_2H_5) etc. Table 3.5 shows the comparison of energy barrier of various isomerization pathwas.

Table 3.5: Comparison of energy barrier for isomerization pathways for all alkenyl radicals. Energy unit: kcal/mol.

	Isomerization to cyclopentane	1,4-H shift	1,5-H shift
$S6XC_8H_{14}-1E7M$	6.2	17.8	-
$P8XC_8H_{14}-2E2M$	-	22.2	12.4
$P8XC_8H_{14}-3E2M$	7.8	16.8	-
$P6XC_6H_{10}-1E5IP$	5.7	16.3	-
$P6XC_6H_{10}-1E4IP$	6.3	19.2	-
$P6XC_6H_{10}-1E3IP$	9.8	17.5	-
$P6XC_6H_{10}-1E2IP$	9.8	17.7	-

3.3.1.6 Stepwise dehydrogenation of cyclic intermediate

Decomposition of alkyl-cyclopentane radicals

From the isomerization of the alkenyl radical, four different alkyl-cyclopentane radicals formed.

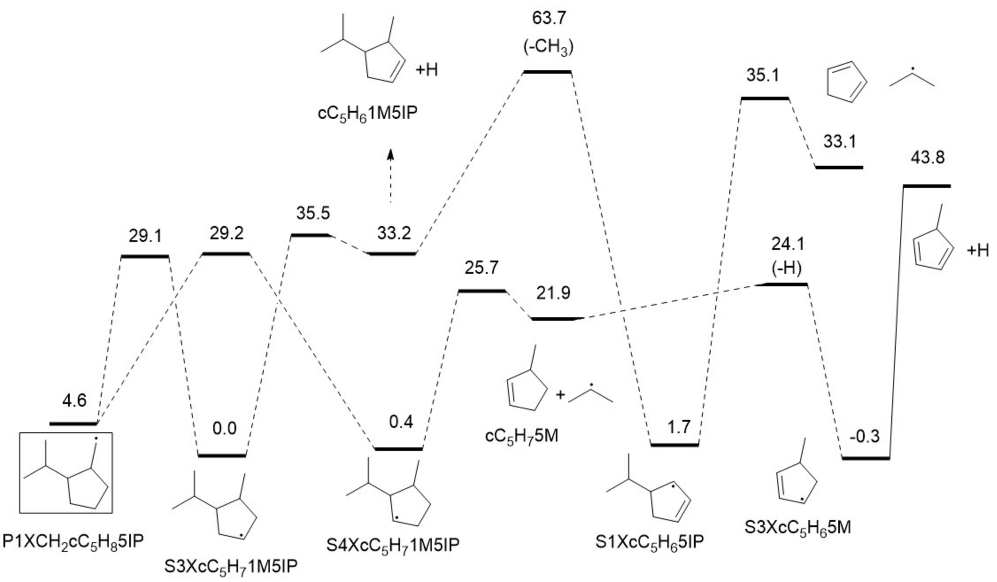

Figure 3.17: Stepwise decomposition of $P1XCH_2cC_5H_85IP$. $(-CH_3)$ indicates CH_3-abstraction reaction by H atom and(-H) indicates H-abstraction reaction by H atom. Energy unit: kcal/mol.

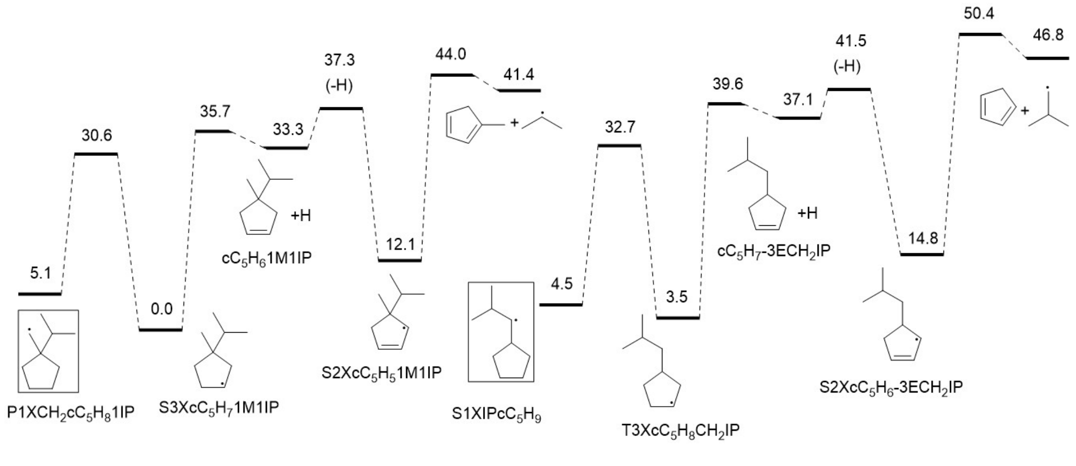

Figure 3.18: Stepwise decomposition of $P1XCH_2cC_5H_81IP$ and $S1XIPcC_5H_9$. (-H) indicates H-abstraction reaction by H atom. Energy unit: kcal/mol.

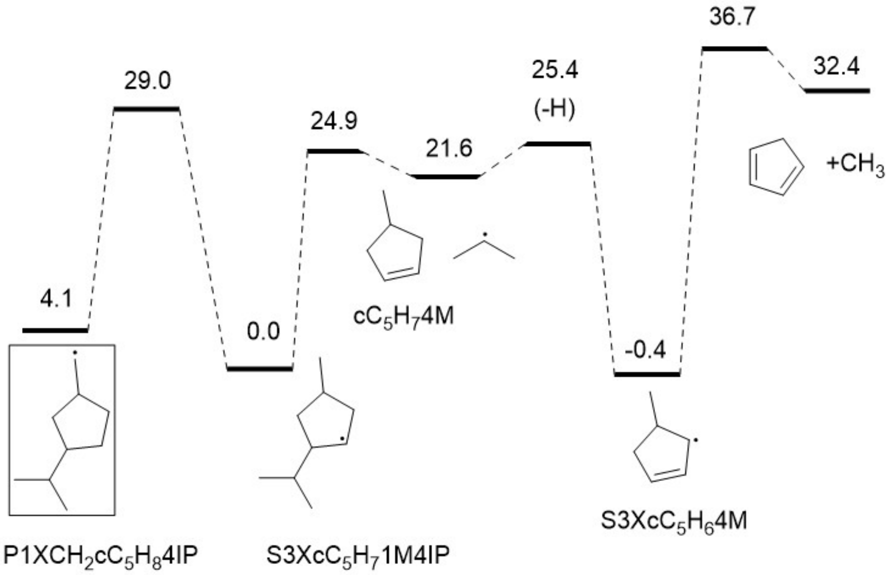

Figure 3.19: Stepwise decomposition of $P1XCH_2cC_5H_84IP$. (-H) indicates H-abstraction reaction by H atom. Energy unit: kcal/mol.

Figure 3.17, figure 3.18, and figure 3.19 illustrate the decomposition of those alkyl-cyclopentane leading to cyclopentadiene and methylcyclopentadiene. All alkyl-cyclopentane radicals first undergo an intermolecular isomerization process to form more stable alkyl-cyclopentane radical through a five-member ring TS. Then subsequent elimination, abstraction-elimination reactions happen, which lead to the formation of either cyclopentadiene or methylcyclopentadiene.

Dehydrogenation of alkyl-cyclohexene

Figure 3.20 and figure 3.21 show the PES of stepwise dehydrogenation of alkyl-cyclohexenes. Alkyl-cyclohexene forms allylic alkyl-cyclohexane radical by H-abstraction reaction followed by the formation of alkyl-cyclohexadiene (by either H-elimination or iso-propyl group elimination). Alkyl-cyclohexadiene then follows a similar pathway to form aromatic products. IPCH-1E and IPCH-2E formed the same alkyl-cyclohexadiene (IPCH-15E) through subsequent H-abstraction and H-elimination reaction. IPCH-15E then leads to iso-propylbenzene (A1IP) which occurs through H-abstraction followed by H-elimination reaction. Alkylcyclohexadiene radical attached to carbon centre near the iso-propyl group are formed with lower energy barrier than the other one, whereas H-elimination from alkylcyclohexadiene radical attached to carbon centre near the isopropyl group associated with higher energy barrier.

On the other hand, IPCH-3E first forms alkylcyclohexene radical (S2XIPCH-

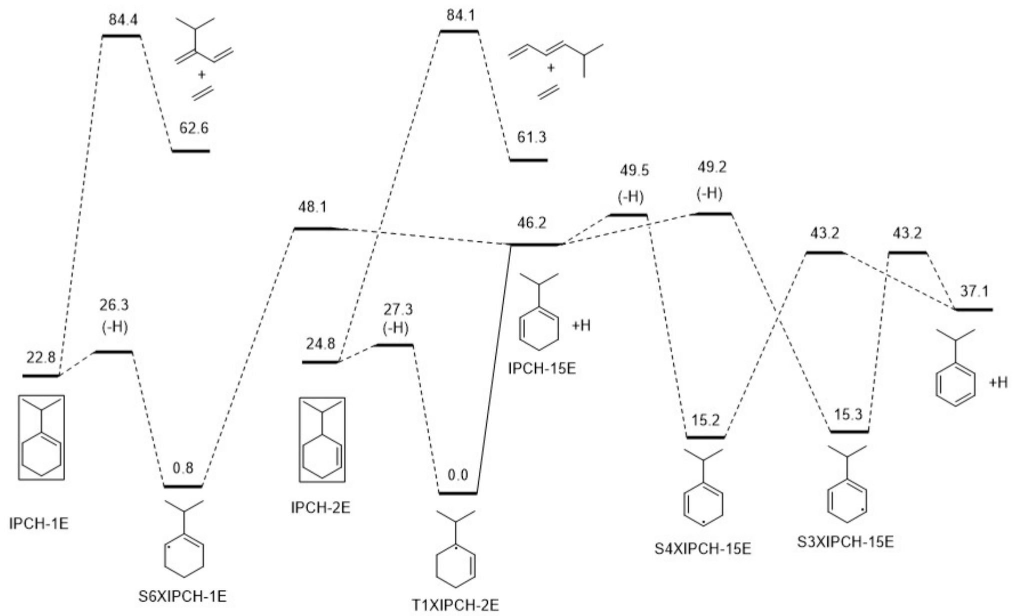

Figure 3.20: Stepwise decomposition of IPCH-1E and IPCH-2E. (-H) indicates H-abstraction reaction by H atom. Solid line indicate barrier less reaction. Energy unit: kcal/mol.

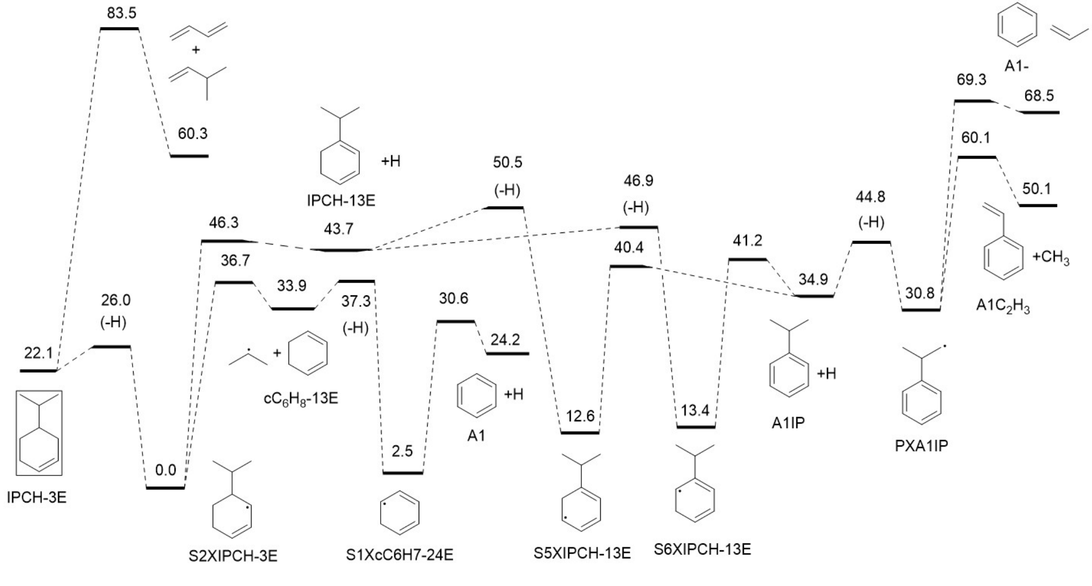

Figure 3.21: Stepwise decomposition of IPCH-3E. (-H) indicates H-abstraction reaction by H atom. Energy unit: kcal/mol.

3E) by H-abstraction which leads to either cyclohexadiene ($cC_6H_8 - 13E$) by iso-propyl group (iC_3H_7) elimination or alkylcyclohexadiene (IPCH-13E) by H-elimination. The iC_3H_7 elimination is more energetically favourable than H-elimination. IPCH-13E/$cC_6H_8 - 13E$ then leads to iso-propyl-benzene(A1IP)/ benzene(A1) after H-abstraction followed by H-elimination. A1IP further decompose to form styrene ($A1C_2H_3$) and benzyl radical(A1-). To understand the effect of the iso-propyl group in the stepwise dehydrogenation, we compare the energy barrier of alkyl-cyclohexene with cyclohexene. In Table 3.6, we can see that the energy barriers for all the reactions for alkyl-cyclohexene are less than those of cyclohexene. The significant difference is seen in iC_3H_7 elimination from IPCH-3E that forms cyclohexadiene.

Table 3.6: Comparison of energy barrier of stepwise dehydrogenation pathways between alkyl-cyclohexene and cyclohexene. For IPCH-3E, the value inside bracket indicates energy barrier of iC_3H_7 elimination. For cyclohexene the energy barrier was recalculated in this study using CBS-QB3 method, from the work of Gong et al[8]. Energy unit: kcal/mol.

	IPCH-1E	IPCH-2E	IPCH-3E	cyclohexene
H-abstraction to form cyclohexene radical	3.5	2.5	3.9	5.4
Elimination reaction to form cyclohexadiene	47.3	46.2	46.3(36.7)	48.5
H-abstraction to form cyclohexadiene radical	3.0	3.0	3.2	3.4
Elimination reaction to form aromatic molecule	27.9	27.9	27.8	28.1

3.3.2 Rate Calculation

We calculate the high-pressure limit (HPL) rate for all the reactions using TST for the reaction with saddle point and VTST for the reaction without saddle point for the temperature range of 800-2000 K.

3.3.2.1 Unimolecular decomposition and isomerization of IPCH

Unimolecular decomposition channel (i.e., CH_3 removal and C_3H_7 elimination channel) is not associated with any saddle point. As such, we did stepwise optimization (relax scan, figure 3.22) to get PES and then calculate rate parameters using VTST. Isomerization of IPCH occurs through two steps (Figure 3.3), and we have calculated rate parameters for both steps. From figure 3.3, we can see that at MRCI method, in some cases, energy of TS of H-migration step (2nd step of isomerization process) is less than that of the biradical intermediate (INT2 to $C_6H_{11}-1E5IP$ and INT3 to $C_6H_{11}-1E5IP$). This was encountered for the isomerization process of methyl-cyclohexane as well. In that study, the authors artificially increased the energy of the corresponding TS[2]. In our study, we did not want to follow this artificial procedure and we used CASSCF energy barriers for 2nd step of the isomerization process. As figure 3.22 shows, the barrier height of the variational transition state varies for CH_3 loss channel from 69.7 to 80.6 kcal/mol with C-C bond stretching 2.7 to 3.3 Å and that for C_3H_7 elimination channel from 63.6-80.3 kcal/mol (with C-C bond stretching 2.6 to 3.5 Å) within the studied temperature range. Comparing the energies of the variational transition state for the CH_3 and C_3H_7 eliminations channels with that of the isomerization channel (Figure 3.3), one cannot neglect those channels.

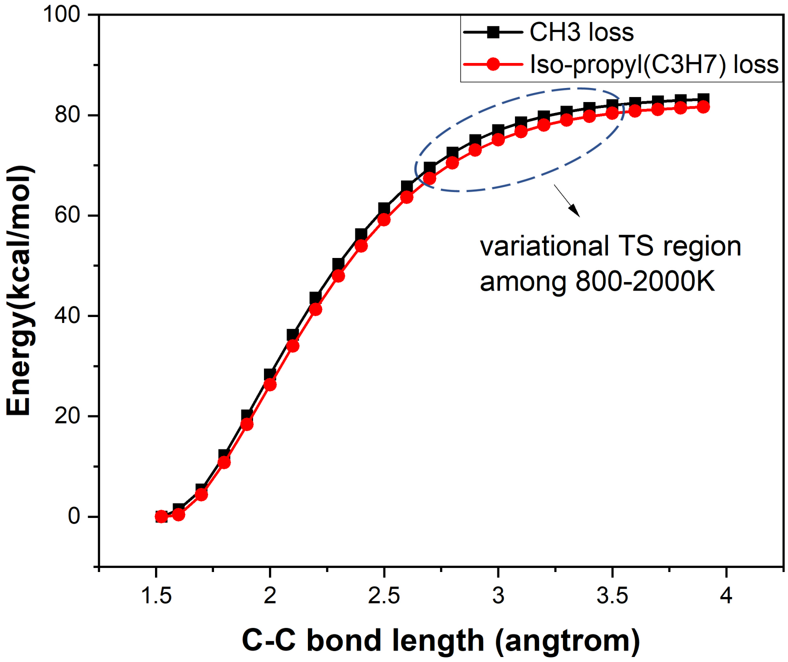

Figure 3.22: Stepwise optimized potential energy curve of IPCH dissociation via CH_3 loss and C_3H_7 loss. Method: MRCI/6-31+g(d,p)//CAS(2,2)/ 6-31+g(d,p).

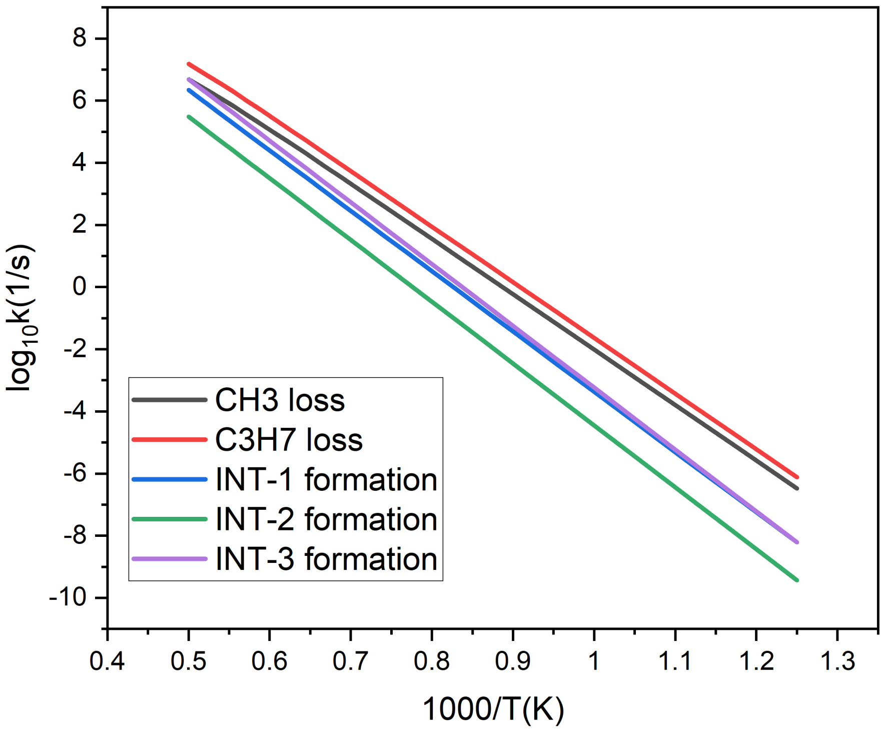

Figure 3.23: HPL rate constant for IPCH decomposition and ring-opening step of isomerization, i.e., first step to form biradical.

From figure 3.23 and figure 3.24, we can see that for all isomerization reactions, the rate constant of the ring-opening step (1st step) to form biradical is much less than that for the H-migration step (2nd step). This result follows the same trend as that of isomerization of methyl-cyclohexane as reported by Wang et al.[2]. The rates of H-migration reaction associated with all biradicals are similar except the reactions associated with INT-1 to form $C_8H_{15} - 2E2M$ (TS is an 8-member cyclic ring associated with high energy barrier) and with INT-3 to form $C_6H_{11} - 1E3IP$ (although TS is a 6-member cyclic ring, the iso-propyl group causes steric hindrance in the cyclic ring resulting in a high energy barrier). The rate constants for formation of INT-1 and INT-3 are higher than that for the formation of INT-2. Moreover, the unimolecular decomposition reactions dominate over isomerization reactions. The dominant reaction channel is the C_3H_7 removal channel, followed by CH_3 elimination. This result also follows the same trend as the unimolecular reaction of methylcyclohexane studied by Wang et al.[2]. From figure 3.25, we can

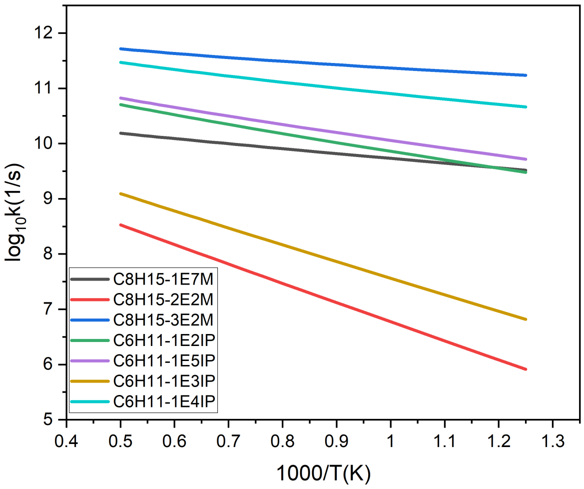

Figure 3.24: HPL rate constant for 2nd step of isomerization of IPCH i.e., intramolecular H-migration from biradical to form alkene.

see that the rate of CH_3 removal from MCH is similar to the rate of C_3H_7 removal from IPCH.

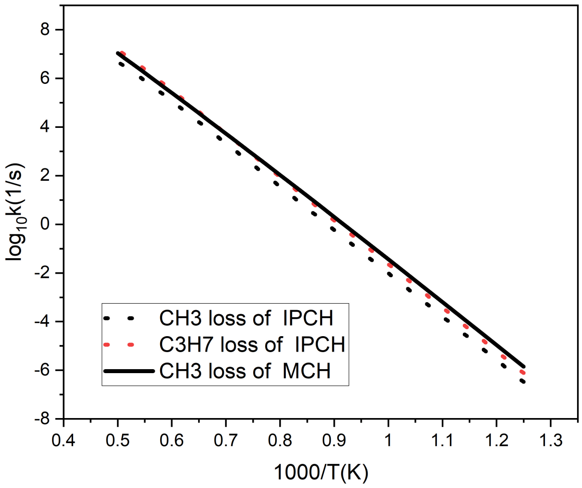

Figure 3.25: Comparison of the rate constant of the decomposition reaction of IPCH and MCH. The solid line is for MCH[2], and the dotted line is for IPCH.

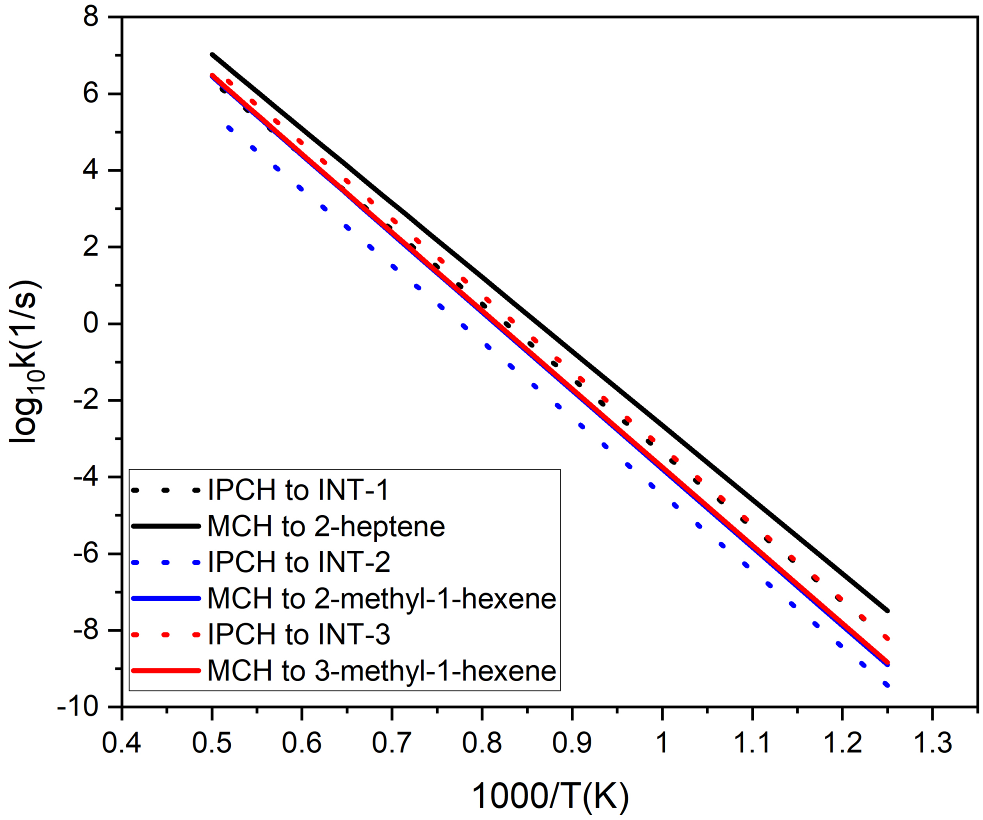

Figure 3.26: Comparison of rate constant of isomerization reaction of IPCH and MCH. The solid line is for MCH[2], and the dotted line is for IPCH. The black line stands for C1-C2 bond breaking, the blue line for C2-C3 bond breaking, and the red line is for C3-C4 bond breaking.

However, the rate of CH_3 removal from IPCH is comparatively smaller. In figure 3.26 we compare the rate of isomerization of MCH with rate of biradical formation of IPCH (with the similar C-C bond breaking). For C1-C2 and C2-C3 bond breaking, rate constant for MCH is greater than that of IPCH whereas for C3-C4 bond braking, rate constant for IPCH is greater than that in MCH.

3.3.2.2 H-abstraction reaction by H atom and CH_3 radical

Figure 3.27 and figure 3.28 show the Arrhenius plot for rate constant of H-abstraction reaction. Rate constant of H-abstraction from IPCH by H atom is higher than

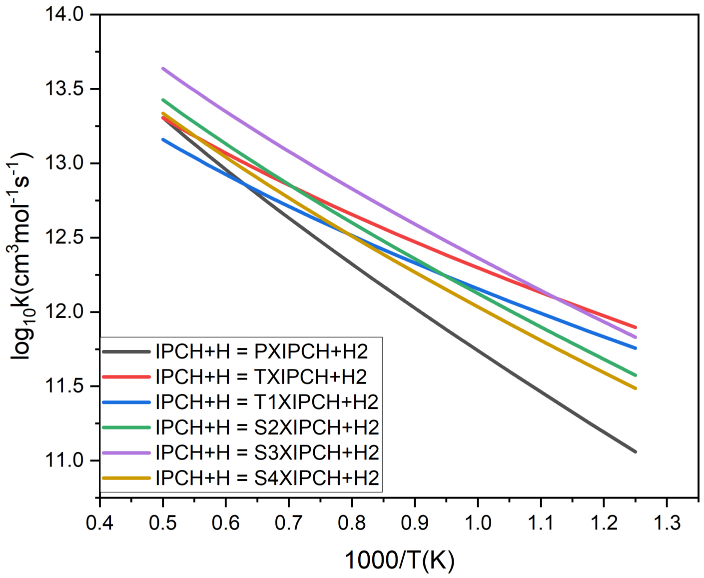

Figure 3.27: Rate constant of H-atom abstraction of IPCH from H atom.

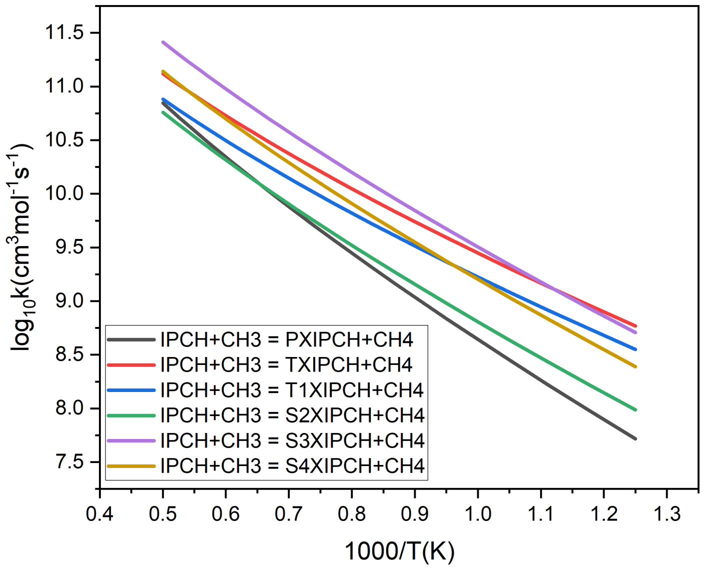

Figure 3.28: Rate constant of H-atom abstraction of IPCH from CH_3 radical.

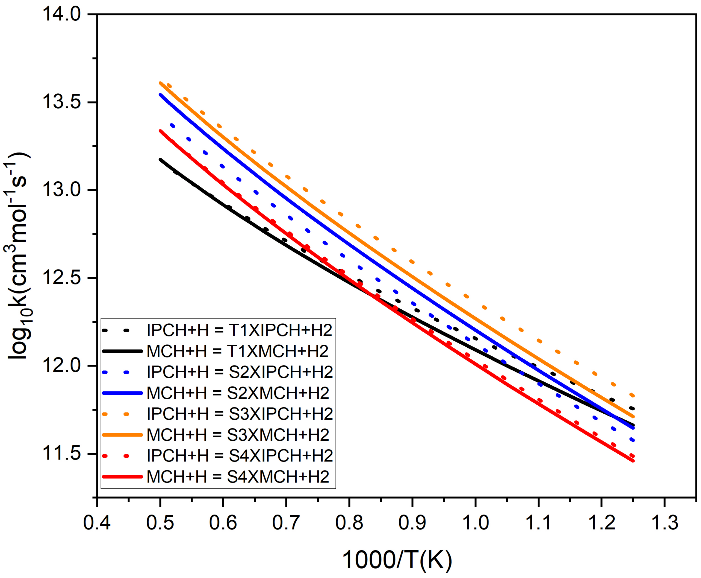

Figure 3.29: Comparison of rate constant of H-abstraction reaction of IPCH and MCH. Solid line is for MCH[4], and dotted line is for IPCH. Black line stand for C1-H abstraction, blue line for C2-H abstraction, orange line for C3-H abstraction and red line is for C4-H abstraction.

the rate constant of H-abstraction from IPCH by CH_3 radical. In both cases, rate constant for H-atom abstraction at the primary carbon is the lowest. In figure 3.29 we compare the rate constants for abstraction reactions from IPCH and MCH.

3.3.3 Kinetic parameters

Kinetic parameters A, and E_a for all the reactions were obtained by fitting the calculated rate constant over the temperature range of 800-2000 K. All the kinetic parameters are listed in table 3.7.

Table 3.7: High pressure limit rate parameter of Iso-propylcyclohexane decomposition reactions.

No	**Reaction**	**A**	E_a
Unimolecular decomposition and isomerization of IPCH			
1	$IPCH = cC_6H_{11} + iC_3H_7$	1.47E+16	81449.4
2	$IPCH = SXC_2H_4cC_6H_{11} + CH_3$	4.23E+15	80690.3
3	$IPCH = int1$	1.11E+16	88829.8
4	$IPCH = int2$	2.75E+15	91017.7
5	$IPCH = int3$	4.33E+16	90940.2
6	$int1 = C_8H_{15} - 1E7M$	4.23E+10	4084.1
7	$int1 = C_8H_{15} - 3E2M$	1.05E+12	2965.3
8	$int1 = C_8H_{15} - 2E2M$	1.84E+10	15967.7
9	$int2 = C_6H_{11} - 1E2IP$	3.21E+11	7516.6
10	$int2 = C_6H_{11} - 1E5IP$	3.51E+11	6783.7
11	$int3 = C_6H_{11} - 1E3IP$	4.02E+10	13908.2
12	$int3 = C_6H_{11} - 1E4IP$	9.76E+11	4949.7
abstraction reaction by H atom and CH_3 radical			
13	$IPCH + H = SXC_2H_4cC_6H_{11} + CH_4$	1.71E+14	35590.8
14	$IPCH + H = PXIPCH + H_2$	5.86E+14	13805.7
15	$IPCH + H = TXIPCH + H_2$	1.61E+14	8684.7
16	$IPCH + H = T1XIPCH + H_2$	1.15E+14	8663.2
17	$IPCH + H = S2XIPCH + H_2$	4.21E+14	11389.8
18	$IPCH + H = S3XIPCH + H_2$	6.40E+14	11125.9
19	$IPCH + H = S4XIPCH + H_2$	3.42E+14	11391.8
20	$IPCH + CH_3 = PXIPCH + CH_4$	7.37E+12	19247.8
21	$IPCH + CH_3 = TXIPCH + CH_4$	4.23E+12	14469.2
22	$IPCH + CH_3 = T1XIPCH + CH_4$	2.40E+12	14369.8
23	$IPCH + CH_3 = S2XIPCH + CH_4$	3.57E+12	17063.3
24	$IPCH + CH_3 = S3XIPCH + CH_4$	1.45E+13	16647.6
25	$IPCH + CH_3 = S4XIPCH + CH_4$	8.26E+12	16918.2

No	Reaction	A	E_a
26	$IPCH + CH_3 = S2XIPCH + CH_4$	3.57E+12	17063.3
27	$IPCH + CH_3 = S3XIPCH + CH_4$	1.45E+13	16647.6
28	$IPCH + CH_3 = S4XIPCH + CH_4$	8.26E+12	16918.2
decomposition and isomerization of alkyl-cyclohexane radicals			
29	PXIPCH = CH2-IPCH+H	6.00E+13	36558.5
30	TXIPCH = CH2-IPCH+H	1.09E+14	38837.8
31	TXIPCH = CH2-2-IPCH+H	6.73E+14	40203
32	T1XIPCH = CH2-2-IPCH+H	5.33E+13	36975.8
33	T1XIPCH = IPCH-1E+H	3.04E+14	37065.3
34	S2XIPCH = IPCH-1E+H	3.72E+13	35986.2
35	S2XIPCH = IPCH-2E+H	2.73E+14	36898.3
36	S3XIPCH = IPCH-2E+H	1.88E+14	37748.9
37	S3XIPCH = IPCH-3E+H	2.20E+14	37587.9
38	S4XIPCH = IPCH-3E+H	2.53E+14	36087.6
39	$SXC_2H_4cC_6H_{11} = CH_2CHcC_6H_{11} + H$	2.75E+13	38245.7
40	$SXC_2H_4cC_6H_{11} = CH_3CHcC_6H_{10} + H$	2.17E+13	37820.4
41	$PXIPCH = CH_2CHcC_6H_{11} + CH_3$	2.67E+14	31415.6
42	$PXIPCH = cC_6H_{11} + C_3H_6$	1.68E+14	26950.4
43	$T1XIPCH = CH_3CHcC_6H_{10} + CH_3$	1.64E+14	30616.8
44	$S2XIPCH = cC_6H_{10} + iC_3H_7$	0.92+14	27693.6
45	$TXIPCH = P8XC_8H_{14} - 2E2M$	2.97E+14	30897
46	$T1XIPCH = P6XC_6H_{10} - 1E2IP$	7.50E+13	31662.1
47	$S2XIPCH = P6XC_6H_{10} - 1E3IP$	6.40E+13	31111.6
48	$S2XIPCH = P8XC_8H_{14} - 3E2M$	6.90E+13	30306.8
49	$S3XIPCH = P6XC_6H_{10} - 1E4IP$	1.22E+14	32524.5
50	$S3XIPCH = S6XC_8H_{14} - 1E7M$	7.30E+13	29120.4
51	$S4XIPCH = P6XC_6H_{10} - 1E5IP$	1.98E+14	32204.6
dissociation of alkene and alkyl-cyclohexene			
52	$IPCH - 1E = C_2H_4 + C_4H_5 - 13E2IP$	1.87E+15	65045

No	**Reaction**	**A**	E_a
53	$IPCH-2E=C_2H_4+C_6H_9-13E5M$	1.15E+15	62642.5
54	$IPCH-3E=C_4H_6+C_4H_7-1E3M$	8.08E+14	64774.8
55	$C_8H_{15}-1E7M+H=S3XC_8H_{14}-1E7M+H_2$	2.24E+14	8247.1
56	$C_8H_{15}-1E7M+CH_3=S3XC_8H_{14}-1E7M+CH_4$	4.65E+08	8374.6
57	$C_8H_{15}-1E7M=C_3H_6+C_5H_9-1E4M$	4.95E+12	55419
58	$C_8H_{15}-1E7M=aC_3H_5+P1XC_5H_{10}4M$	1.33E+14	63602.3
59	$C_8H_{15}-3E2M+H=S5XC_8H_{14}-3E2M+H_2$	2.42E+11	5397.4
60	$C_8H_{15}-3E2M+CH_3=S5XC_8H_{14}-3E2M+CH_4$	3.18E+12	13386.4
61	$C_8H_{15}-3E2M=C_3H_6+C_5H_9-2E4M$	1.16E+15	109252.3
62	$C_8H_{15}-3E2M=C_3H_6+C_5H_9-1E4M$	5.73E+12	56961.1
63	$C_8H_{15}-3E2M=nC_3H_7+P1XC_5H_8-2E4M$	1.90E+15	68572.3
64	$C_8H_{15}-2E2M+H=S4XC_8H_{14}-2E2M+H_2$	2.40E+14	7480.4
65	$C_8H_{15}-2E2M+CH_3=S4XC_8H_{14}-2E2M+CH_4$	1.91E+12	12610.4
66	$C_8H_{15}-2E2M=C_4H_8-1+C_4H_7-2E2M$	1.95E+15	108489.2
67	$C_8H_{15}-2E2M=C_4H_8-1+C_4H_7-1E3M$	5.31E+12	57507.6
68	$C_8H_{15}-2E2M=pC_4H_9+P4XC_4H_6-2E2M$	2.25E+15	66191.6
69	$C_6H_{11}-1E2IP+H=S3XC_6H_{10}-1E2IP+H_2$	1.56E+14	7994.9
70	$C_6H_{11}-1E2IP+CH_3=S3XC_6H_{10}-1E2IP+CH_4$	1.14E+12	13017.4
71	$C_6H_{11}-1E2IP=C_3H_6+C_4H_6-1E23M$	6.59E+12	55162.7
72	$C_6H_{11}-1E2IP=nC_3H_7+P1XCH_2C_4H_6-1E3M$	2.09E+15	66986.5
73	$C_6H_{11}-1E5IP+H=S3XC_6H_{10}-1E5IP+H_2$	5.10E+15	11236.2
74	$C_6H_{11}-1E5IP+CH_3=S3XC_6H_{10}-1E5IP+CH_4$	4.10E+13	16489.6
75	$C_6H_{11}-1E5IP=C_3H_6+C_4H_6-1E23M$	1.11E+14	55272
76	$C_6H_{11}-1E5IP=aC_3H_5+P1XC_4H_723M$	3.72E+16	69110.8
77	$C_6H_{11}-1E3IP+H=T3XC_6H_{10}-1E3IP+H_2$	2.22E+14	8814.2
78	$C_6H_{11}-1E3IP+CH_3=T3XC_6H_{10}-1E3IP+CH_4$	1.24E+12	14405.2
79	$C_6H_{11}-1E3IP=C_3H_6+C_5H_9-2E4M$	3.97E+12	53586.8
80	$C_6H_{11}-1E3IP=C_3H_6+C_6H_{12}-2E$	2.91E+13	55132.9
81	$C_6H_{11}-1E3IP=iC_3H_7+S3XC_6H_{11}-1E$	6.19E+14	62634.6

No	**Reaction**	**A**	E_a
82	$C_6H_{11}-1E3IP=nC_3H_7+S3XC_5H_8-1E4M$	1.65E+14	64625.7
83	$C_6H_{11}-1E4IP+H=S3XC_6H_{10}-1E4IP+H_2$	2.13E+14	9020.5
84	$C_6H_{11}-1E4IP+CH_3=S3XC_6H_{10}-1E4IP+CH_4$	1.24E+12	14520.7
85	$C_6H_{11}-1E4IP=C_3H_6+C_5H_9-2E2M$	2.55E+15	104278.3
86	$C_6H_{11}-1E4IP=C_3H_6+C_5H_9-2E4M$	7.33E+12	57563.2
87	$C_6H_{11}-1E4IP=aC_3H_5+S3XC_5H_{10}2M$	3.20E+14	63175.1
decomposition and isomerization of alkenyl radicals			
88	$S6XC^8H_{14}-1E7M=S7XC_8H_{14}-1E7M$	8.86E+12	39591
89	$S6XC_8H_{14}-1E7M=S5XC_8H_{14}-1E7M$	5.99E+12	40073.9
90	$S6XC_8H_{14}-1E7M=S4XC_8H_{14}-1E7M$	3.75E+12	41288.1
91	$S6XC_8H_{14}-1E7M=S3XC_8H_{14}-1E7M$	1.70E+11	19827.5
92	$S6XC_8H_{14}-1E7M=P8XC_8H_{14}-1E7M$	5.24E+12	43070.8
93	$S7XC_8H_{14}-1E7M=iC_4H_8+P5XC_5H_9-1E$	1.61E+15	64774.8
94	$S6XC_8H_{14}-1E7M=CH_3+C_8H_{14}-16E$	5.02E+13	31473.3
95	$S6XC_8H_{14}-1E7M=C_4H_7-1E3M+C_4H_7$	1.76E+14	31270.8
96	$S5XC_8H_{14}-1E7M=iC_3H_7+C_6H_{10}-15E$	1.13E+14	29438.4
97	$S5XC_8H_{14}-1E7M=aC_3H_5+C_5H_9-1E4M$	2.64E+13	22944.2
98	$S4XC_8H_{14}-1E7M=iC_4H_9+C_5H_8-14E$	1.43E+14	31604.4
99	$S4XC_8H_{14}-1E7M=C_2H_3+C_6H_{11}-1E5M$	1.89E+14	38619.2
100	$S3XC_8H_{14}-1E7M=C_4H_6+P4XC_4H_83M$	1.12E+15	39587
101	$P8XC_8H_{14}-1E7M=CH_3+C_8H_{14}-17E$	2.51E+14	33953.3
102	$P8XC_8H_{14}-1E7M=C_3H_6+P6XC_6H_{11}-1E$	2.57E+14	31562.7
103	$S6XC_8H_{14}-1E7M=P1XCH_2cC_5H_85IP$	2.09E+10	7160.5
104	$P8XC_8H_{14}-2E2M=S7XC_8H_{14}-2E2M$	4.25E+13	40614.4
105	$P8XC_8H_{14}-2E2M=S6XC_8H_{14}-2E2M$	1.62E+13	40064
106	$P8XC_8H_{14}-2E2M=S5XC_8H_{14}-2E2M$	1.97E+12	23242.3
107	$P8XC_8H_{14}-2E2M=S4XC_8H_{14}-2E2M$	1.50E+11	13043.8
108	$S7XC_8H_{14}-2E2M=C_3H_6+P5XC_5H_8-2E2M$	1.33E+14	29919.3
109	$S6XC_8H_{14}-2E2M=CH_3+C_7H_{11}-15E6M$	5.43E+13	31650.1

No	**Reaction**	**A**	E_a
110	$S6XC_8H_{14}-2E2M=C_4H_8-1+P4XC_4H_6-2E2M$	1.80E+13	21177.6
111	$S5XC_8H_{14}-2E2M=iC_4H_7-1+C_5H_{10}-1E$	1.18E+14	38341.0
112	$S5XC_8H_{14}-2E2M=C_2H_5+C_6H_9-14E5M$	9.41E+13	30410.1
113	$S4XC_8H_{14}-2E2M=nC_3H_7+C_5H_7-13E4M$	1.31E+15	40040.1
114	$P8XC_8H_{14}-2E2M=C_2H_4+P6XC_6H_{10}-2E2M$	3.42E+14	30662.5
115	$P8XC_8H_{14}-3E2M=S7XC_8H_{14}-3E2M$	2.30E+13	40525
116	$P8XC_8H_{14}-3E2M=S6XC_8H_{14}-3E2M$	1.02E+13	40827
117	$P8XC_8H_{14}-3E2M=S5XC_8H_{14}-3E2M$	8.23E+11	18331.7
118	$S7XC_8H_{14}-3E2M=C_3H_6+P1XC_5H_8-2E4M$	3.36E+13	21660.5
119	$S6XC_8H_{14}-3E2M=C_7H_{11}-14E6M+CH_3$	8.11E+13	31922.4
120	$S6XC_8H_{14}-3E2M=C_4H_8-1+S1XC_4H_6-1E3M$	2.46E+14	39070.3
121	$S5XC_8H_{14}-3E2M=C_2H_5+C_6H_9-13E5M$	4.59E+14	40185.2
122	$P8XC_8H_{14}-3E2M=C_2H_4+P1XC_6H_{10}-3E5M$	2.93E+14	31433.5
123	$P8XC_8H_{14}-3E2M=S1XIPcC_5H_9$	2.24E+11	8455.7
124	$P6XC6H_{10}-1E5IP=T5XC_6H_{10}-1E5IP$	4.09E+13	38585.5
125	$P6XC_6H_{10}-1E5IP=S4XC_6H_{10}-1E5IP$	2.56E+13	39920.7
126	$P6XC_6H_{10}-1E5IP=S3XC_6H_{10}-1E5IP$	1.27E+12	17639.2
127	$T5XC_6H_{10}-1E5IP=C_7H_{11}-15E5M+CH_3$	1.18E+14	31177.2
128	$T5XC_6H_{10}-1E5IP=C_4H_6-1E23M+aC_3H_5$	6.05E+13	21280.9
129	$S4XC_6H_{10}-1E5IP=C_7H_{11}-14E6M+CH_3$	4.90E+13	32027.7
130	$S4XC_6H_{10}-1E5IP=C_6H_{10}-14E+iC_3H_7$	2.87E+13	25664.7
131	$S4XC_6H_{10}-1E5IP=C_5H_8-1E34M+C_2H_3$	3.18E+14	38345
132	$S3XC_6H_{10}-1E5IP=S2XC_4H_83M+C_4H_6$	7.87E+14	38092.6
133	$P6XC_6H_{10}-1E5IP=iC_3H_7+C_6H_{10}-15E$	1.16E+14	25903.2
134	$P6XC_6H_{10}-1E5IP=C_4H_7-1E3M+C_4H_7$	1.56E+14	29519.9
135	$P6XC_6H_{10}-1E5IP=P1XCH_2cC_5H_84IP$	2.03E+11	6033.9
136	$P6XC_6H_{10}-1E4IP=T4XC_6H_{10}-1E4IP$	6.24E+14	39197.5
137	$P6XC_6H_{10}-1E4IP=S5XC_6H_{10}-1E4IP$	2.09E+15	42259.8
138	$P6XC_6H_{10}-1E4IP=S3XC_6H_{10}-1E4IP$	2.23E+13	22254.7

No	**Reaction**	**A**	E_a
139	$T4XC_6H_{10} - 1E4IP = C_6H_9 - 14E4Et + CH_3$	9.21E+13	31026.2
140	$T4XC_6H_{10}1E4IP = C_5H_7 - 14E2IP + CH_3$	1.30E+14	31268.6
141	$T4XC_6H_{10} - 1E4IP = C_4H_7 - 1E2IP + C_2H_3$	6.44E+14	39273
142	$S5XC_6H_{10} - 1E4IP = C_6H_{10} - 14E + iC_3H_7$	6.17E+13	26807.3
143	$S5XC6H10 - 1E4IP = C5H9 - 2E4M + aC3H5$	1.16E+13	19403.6
144	$S3XC_6H_{10} - 1E4IP = C_6H_{10} - 13E + iC_3H_7$	1.82E+14	33470.4
145	$S3XC_6H_{10} - 1E4IP = C_6H_9 - 13E5M + C_2H_5$	1.36E+14	37530.3
146	$P6XC_6H_{10} - 1E4IP = S4XC_6H_{10} - 1E5M + C_2H_4$	1.18E+14	31177.2
147	$P6XC_6H_{10} - 1E4IP = P1XCH_2cC_5H_84IP$	1.23E+13	8551.9
148	$P6XC_6H_{10} - 1E3IP = T3XC_6H_{10} - 1E3IP$	2.39E+11	18305.3
149	$P6XC_6H_{10} - 1E3IP = S5XC_6H_{10} - 1E3IP$	2.81E+13	40542.9
150	$P6XC_6H_{10} - 1E3IP = S4XC_6H_{10} - 1E3IP$	4.53E+12	38309.2
151	$T3XC_6H_{10} - 1E3IP = C_5H_7 - 13E3C_3H_7 + CH_3$	4.74E+14	39004.8
152	$T3XC_6H_{10} - 1E3IP = C_4H_5 - 13E2IP + C_2H_5$	3.04E+15	40562.7
153	$S5XC_6H_{10} - 1E3IP = S3XC_5H_8 - 1E4M + C_3H_6$	4.51E+13	21133.9
154	$S4XC_6H_{10} - 1E3IP = C_6H_{11} - 3E2M + C_2H_3$	1.91E+14	38627.2
155	$S4XC_6H_{10} - 1E3IP = C_6H_{10} - 13E + iC_3H_7$	2.20E+13	24969.2
156	$S4XC_6H_{10} - 1E3IP = C_5H_7 - 14E3IP + CH_3$	5.02E+13	31679.9
157	$P6XC_6H_{10} - 1E3IP = P4XC_4H_6 - 1E3IP + C_2H_4$	1.40E+14	30376.3
158	$P6XC_6H_{10} - 1E3IP = P1XCH_2cC_5H_85IP$	2.51E+10	9310.4
159	$P6XC_6H_{10} - 1E2IP = S5XC_6H_{10} - 1E2IP$	2.41E+13	40515
160	$P6XC_6H_{10} - 1E2IP = S4XC_6H_{10} - 1E2IP$	9.13E+12	39644.6
161	$P6XC_6H_{10} - 1E2IP = S3XC_6H_{10} - 1E2IP$	5.31E+11	18726.6
162	$S5XC_6H_{10} - 1E2IP = C_3H_6 + P3XC_3H_4 - 1E2IP$	4.47E+13	21378.3
163	$S4XC_6H_{10} - 1E2IP = C_5H_7 - 14E2IP + CH_3$	7.69E+13	31805.1
164	$S4XC_6H_{10} - 1E2IP = C_4H_8 - 1 + T2XC_4H_6 - 1E3M$	1.17E+14	35322.5
165	$S3XC_6H_{10} - 1E2IP = C_4H_5 - 13E2IP + C_2H_5$	5.45E+13	36155.1
166	$P6XC_6H_{10} - 1E2IP = C_2H_4 + P4XC_4H_6 - 1E2IP$	2.70E+14	30483.6
167	$P6XC_6H_{10} - 1E2IP = P1XCH_2cC_5H_81IP$	3.08E+10	7584.9

No	**Reaction**	**A**	E_a
stepwise dehydrogenation of cyclic intermediate			
decomposition of alkyl-cyclopentane radicals			
168	$S1XIPcC_5H_9 = T3XcC_5H_8CH_2IP$	5.37E+10	29160.2
169	$T3XcC_5H_8CH_2IP = cC_5H_7 - 3ECH_2IP + H$	8.33E+13	38714.6
170	$cC_5H_7 - 3ECH_2IP + H = S2XcC_5H_6 - 3ECH_2IP + H_2$	2.42E+14	8338.9
171	$cC_5H_7 - 3ECH_2IP + CH_3 = S2XcC_5H_6 - 3ECH_2IP + CH_4$	4.20E+12	13266.1
172	$S2XcC_5H_6 - 3ECH_2IP = C_5H_6 + iC_4H_9$	7.26E+14	38611.3
173	$P1XCH_2cC_5H_85IP = S3XcC_5H_71M5IP$	1.12E+12	25833.6
174	$P1XCH_2cC_5H85IP = S4XcC_5H_71M5IP$	1.78E+12	25978.7
175	$S3XcC_5H_71M5IP = cC_5H_61M5IP + H$	7.27E+13	38058.9
176	$cC_5H_61M5IP + H = S1XcC_5H_65IP + CH_4$	2.54E+14	33613.5
177	$S1XcC_5H_65IP = C_5H_6 + iC_3H_7$	3.23E+14	34784
178	$S4XcC_5H_71M5IP = cC_5H_75M + iC_3H_7$	1.31E+14	26121.7
179	$cC_5H_75M + H = cC_5H_7 + CH_4$	6.64E+13	32210.5
180	$cC_5H_75M + H = S3XcC_5H_65M + H_2$	1.36E+14	5527.6
181	$cC_5H_75M + CH_3 = S3XcC_5H_65M + CH_4$	2.16E+12	11079.8
182	$S3XcC_5H_65M = cC_5H5 - 13E5M + H$	1.31E+14	49034.2
183	$P1XCH_2cC_5H_84IP = S3XcC_5H_71M4IP$	1.16E+12	26229.1
184	$S3XcC_5H_71M4IP = cC_5H_74M + iC_3H_7$	1.30E+14	25487.8
185	$cC_5H_74M + H = S3XcC_5H_64M + H_2$	1.24E+14	7292.9
186	$cC_5H_74M + CH_3 = S3XcC_5H_64M + CH_4$	2.30E+12	12824.8
187	$S3XcC_5H_64M = C_5H_6 + CH_3$	4.34E+14	39489.6
188	$S3XcC5H64M = cC5H5 - 13E1M + H$	9.76E+13	45890.4
189	$P1XCH_2cC_5H_81IP = S3XcC_5H_71M1IP$	1.00E+12	24812.2
190	$S3XcC_5H_71M1IP = cC_5H_61M1IP + H$	1.02E+14	38311.2
191	$cC_5H_61M1IP + H = S2XcC_5H_51M1IP + H_2$	4.03E+14	7510.4
192	$cC_5H_61M1IP + CH_3 = S2XcC_5H_51M1IP + CH_4$	3.36E+12	12659.1
193	$S2XcC_5H_51M1IP = cC_5H_5 - 13E1M + iC_3H_7$	1.46E+14	32685.5
194	$cC_5H_5 - 13E5M = cC_5H_5 - 13E1M$	1.50E+13	24466.4

No	**Reaction**	**A**	E_a
decomposition of alkyl-cyclohexene			
195	$IPCH-1E+H=S6XIPCH-1E+H_2$	2.69E+14	7009.3
196	S6XIPCH-1E = IPCH-15E+H	5.79E+14	50564.3
197	$IPCH-15E+H=S4XIPCH-15E+H_2$	3.52E+14	6674.4
198	$IPCH-15E+H=S3XIPCH-15E+H_2$	3.61E+14	6350.3
199	S4XIPCH-15E = A1IP+H	1.72E+14	30390.3
200	S3XIPCH-15E = A1IP+H	1.24E+14	30322.7
201	$A1IP+H=PXA1IP+H_2$	9.31E+14	13611.3
202	$PXA1IP=A1-+C_3H_6$	1.14E+15	40940.3
203	$PXA1IP=A1C_2H_3+CH_3$	6.33E+14	32466.9
204	$IPCH-2E+H=T1XIPCH-2E+H_2$	1.33E+14	5993.2
205	T1XIPCH-2E = IPCH-15E+H	1.81E+14	48074.3
206	$IPCH-3E+H=S2XIPCH-3E+H_2$	1.20E+14	7417.4
207	S2XIPCH-3E = IPCH-13E+H	1.35E+14	49221.0
208	$S2XIPCH-3E=cC_6H_8-13E+iC_3H_7$	5.49E+14	39370.4
209	$IPCH-13E+H=S5XIPCH-13E+H_2$	4.85E+14	10420.5
210	$IPCH-13E+H=S6XIPCH-13E+H_2$	2.88E+14	6558.0
211	S5XIPCH-13E = A1IP+H	1.94E+14	30296.9
212	S6XIPCH-13E = A1IP+H	1.74E+14	30225.3

Note $k(T)=A\exp(-E_a/RT)$, unit is cm^3, mol, s, cal.

3.3.4 Experiment and Simulation

The pyrolysis experiments have been carried out for temperature ranging from 923-1526 K and pressure ranging from 9.8–20.2 bar. The observed dwell times in the present study were in the range of 1.39-1.54 msec. The gas chromatograms of post shock mixture of IPCH obtained using GC-FID/FID for one typical experiment are shown in figure 3.30 and figure 3.31.

The major products observed in the post shock mixture have been the following: methane, ethene, acetylene, ethane, propene, allene, propyne, vinylacetylene, 1,3-butadiene, pentadiene, cyclopentadiene, benzene.

The minor products are the following: propane, butene, 1,3-butadiyne, butyne, methylbutadiene, methylpentadiene, methylcyclopentadiene, cyclohexadiene, cyclohexene, toluene, styrene, and ethylidenecyclohexane.

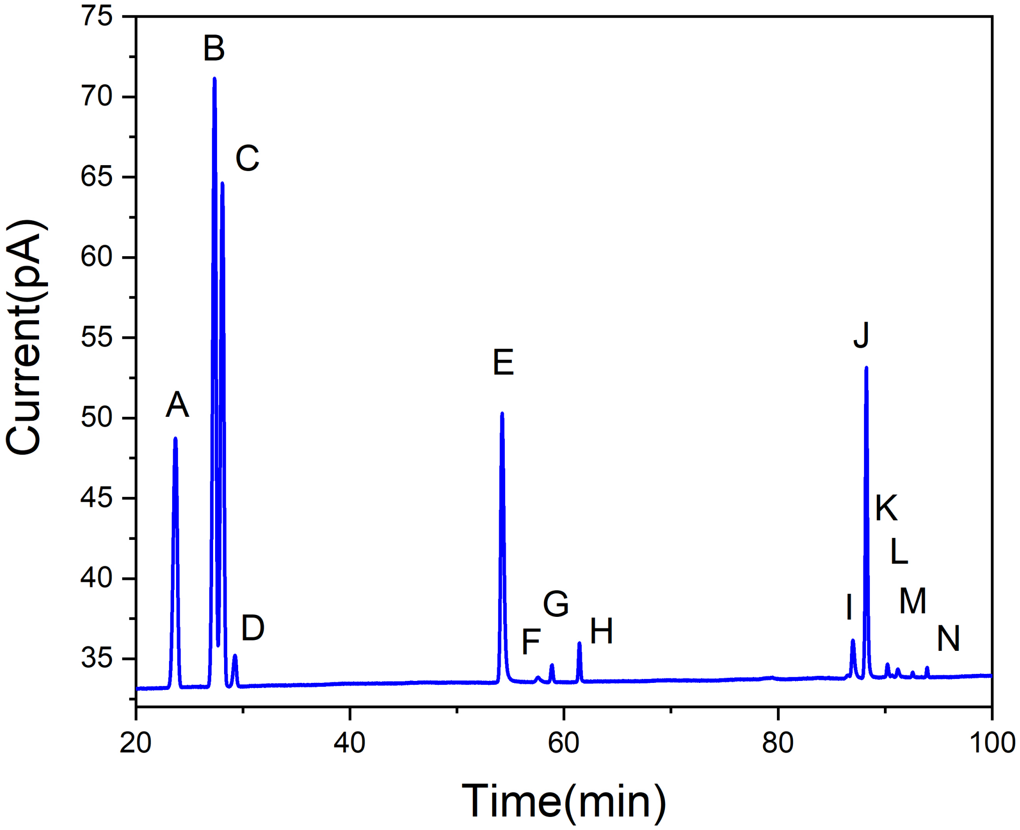

Figure 3.30: Chromatogram from GC front-FID (lower boiler species). Peaks are assigned to (A) methane, (B) ethene, (C) acetylene, (D) ethane, (E) propene, (F) propane, (G) allene, (H) propyne, (I) vinylacetylene, (J) 1,3-butadiene, (K) 1,3-butadiyne, (L) 2-butayne, (M) 1,3-butadiene-2-methyl, (N) 1-butyne.

We used the 'carbon balance method' to estimate initial reaction concentration with the assumption of the entire carbon was recovered in the gas phase which is reasonable as no solid residues were found[9–12]. We have found this to be an accurate method to calculate initial concentration.

$$[IPCH]_0 = [IPCH]_t + \sum_{i=1}^{27} \frac{n_i[P_i]_t}{9} \tag{3.1}$$

Here, $[IPCH]_0$ is the initial concentration of IPCH, $[IPCH]_t$ is the concentration of IPCH after time t, n_i is the no. of carbon in the ith product, $[P_i]_t$ is

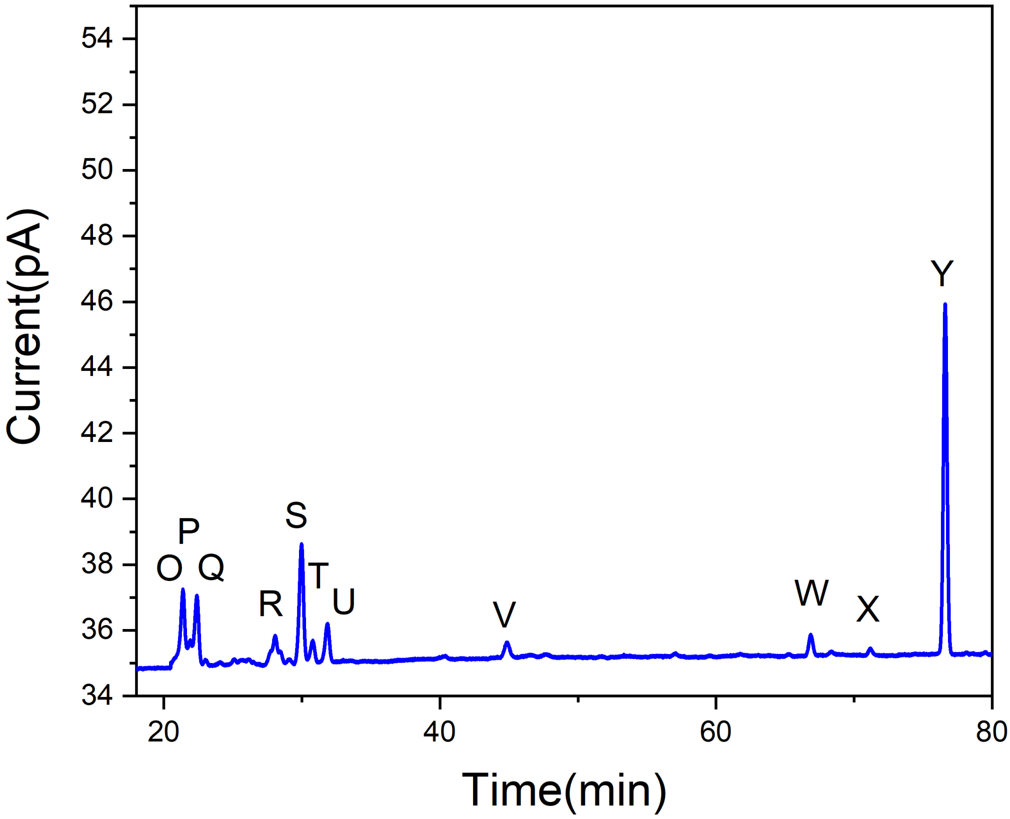

Figure 3.31: Chromatogram from GC back-FID (higher boiler species). Peaks are assigned to (O) 1,3-pentadiene, (P) 1,4-pentadiene, (Q) cyclopentadiene, (R) methylcyclopentadiene, (S) benzene, (T) cyclohexadiene, (U) cyclohexene, (V) toluene, (W) ethylidenecyclohexane, (X) styrene, and (Y) IPCH.

the concentration of the ith product after time t. The distribution of the normalized concentration of the reactants and all the products in the experimental temperature range shown in the next sections.

3.3.4.1 Major species

Figure 3.32 shows the normalized mole fractions profiles for the major species. The product concentration profiles show that ethene is the most abundant product formed by the decomposition of IPCH. After ethane, the concentration of methane and acetylene are also found to be in abundance. The present kinetic model reasonably predicts the decomposition of IPCH and formation of all the major products. IPCH (fig 3.32(a)) start to decompose around 1050 K and is found to completely decompose at the temperature above 1500 K.

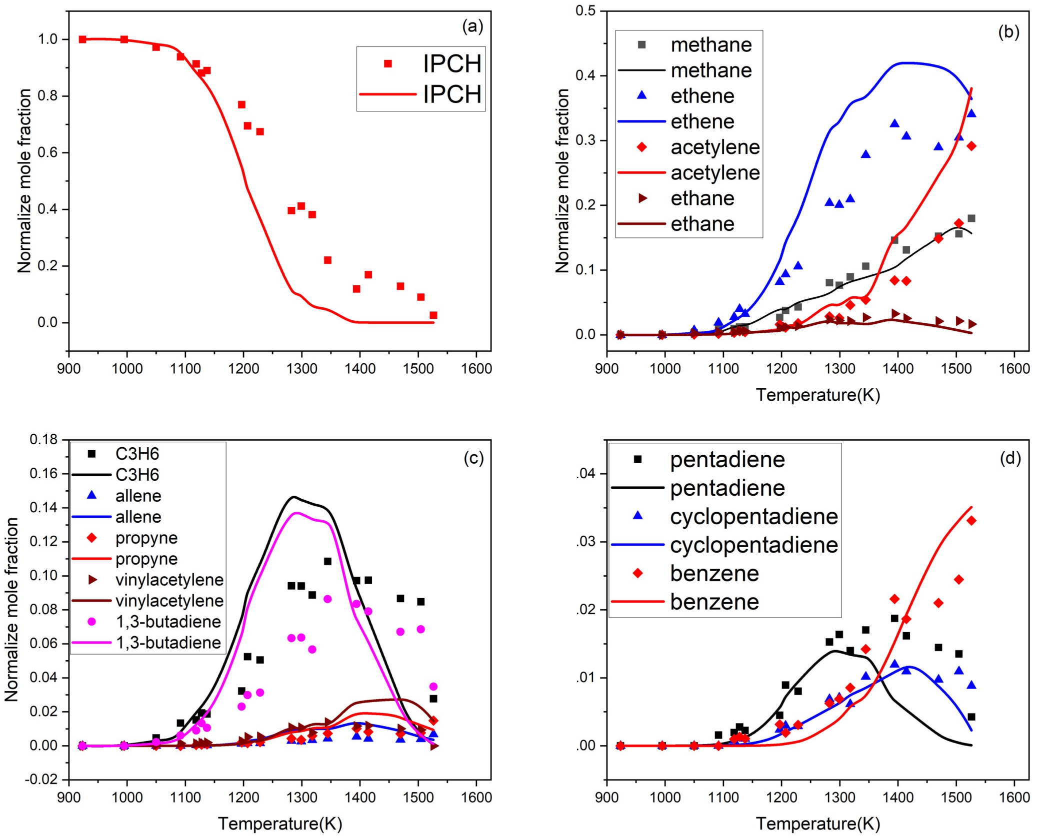

Figure 3.32: Experimental (symbols) and modelling (lines) results of (a) IPCH, (b) methane, ethene, acetylene, ethane, (c) propane, allene, propyne, vinylacetylene, butadiene, (d) pentadiene, cyclopentadiene and benzene (major species). Normalized mole fraction for reactant $= \frac{[IPCH]_t}{k[IPCH]_0}$. Normalization mole fraction for products $= \frac{[P_i]_t}{k[IPCH]_0}$. $k = \frac{[IPCH]_t}{[IPCH]_0} + \sum_i^{27} \frac{[P_i]_t}{[IPCH]_0}$.

Our model overestimates the decomposition of IPCH slightly at the temperature above 1250K. Methane (fig 3.32(b)) starts forming at temperature around 1050 K and its concentration increases with temperature. Our kinetic model predicts the formation of methane very well. Ethene (fig 3.32(b)) also starts forming around 1050 K temperature and plateauing around 1400 K before decreasing slowly with temperature. Present model predicts well for ethene for both peak temperature and the trend of formation over the temperature range. Acetylene (fig 3.32(b)) is the other important product which also starts forming around 1050 K. Present model over-predicts the concentration of acetylene at temperature above 1400 K. Ethane (fig 3.32(b)) also starts forming at the same temperature as methane but amount of ethane formed is very less compared to that of methane. Both propene (C_3H_6) and 1,3-butadiene (fig 3.32(c)) start forming at the temperature around 1100K and hit the peak at the temperature around 1350K. Present model underpredicts the formation of both propene and 1,3-butadiene at high temperature (above 1400K). Allene, propyne and vinylacetylene (fig 3.32(c)) start forming at temperature above 1200 K, though their concentrations are very small. Present model predicts the trend of formation of them too very well over the temperature range. Benzene (fig 3.32(d)) is the most abundant aromatic product which starts forming around 1250 K and its concentration keeps on increasing up to the highest temperature extreme in the current study. Our kinetic model predicts this trend quite well. Cyclopentadiene (fig 3.32(d)) is another important cyclic product which also starts forming at the same temperature as that of benzene formation (1250 K) and hit peak at 1400 K. Its concentration stays constant with the temperature within the T range in our study. Our kinetic model underestimates the formation of cyclopentadiene beyond 1400K temperature. Both 1,3-pentadiene and 1,4-pentadiene have been found in small amounts and their mole fraction sum is presented as the total concentration of pentadiene in figure 3(d). The present kinetic model underpredicts the formation of pentadiene slightly at high temperature.

3.3.4.2 Minor species

Figure 3.33 shows the normalized mole fraction profile for the minor species. Propane (fig 3.33(a)) is the longest chain and the least abundant saturated hydrocarbon we detected in our experiment. It starts forming around 1200 K, hit the peak around 1350 K and then start decreasing with temperature. Our kinetic model underestimates propane. Butene and methylbutadiene (fig 3.33(a)) are overestimated by our model in the temperature range of 1150-1450 K whereas butadiyne is overestimated mostly at the temperature above 1450 K. Toluene and styrene (fig 3.33(b)) are the other two aromatic product we have detected in our experiment. The formation of toluene starts at the temperature around 1300 K whereas the formation of styrene begins to appear around 1400 K. Formation of both these products increase with the increase of temperature. Our kinetic model aggresses reasonably with the experimental trend when it comes to the formation of these aromatic products. Methylcyclopentadiene, methylpentadiene (fig 3.33(b)) are overestimated by the present kinetic model. We detected few other cyclic six-member ring species (fig 3.33(c)) (namely, cyclohexene, cyclohexadiene

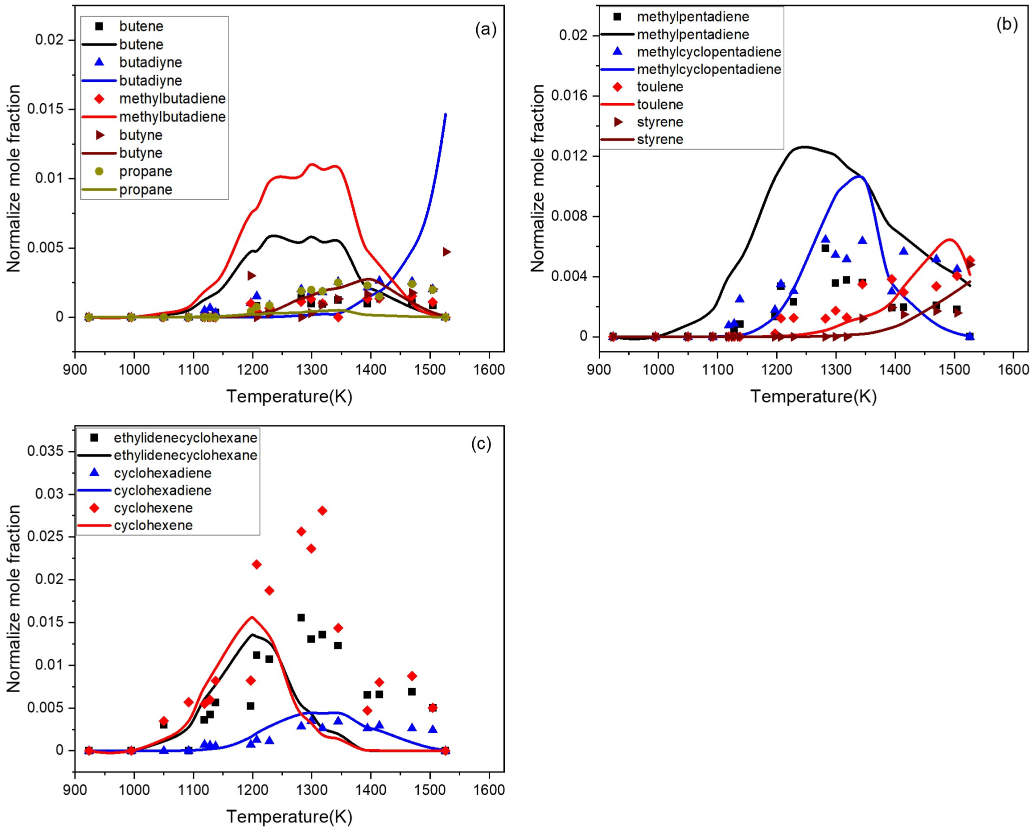

Figure 3.33: Experimental (symbols) and modelling (lines) results of (a) propane, butene, butadiyne, butyne, methylbutadiene, (b) methylpentadiene, methylcyclopentadiene, toluene, styrene, (c) cyclohexadiene, cyclohexene, and ethylidenecyclohexane (minor species). Normalization mole fraction = $\frac{[P_i]_t}{k[IPCH]_0}$. $k = \frac{[IPCH]_t}{[IPCH]_0} + \sum_i^{27} \frac{[P_i]_t}{[IPCH]_0}$.

and ethylidenecyclohexane). All these species start forming around 1100 K temperature. The concentration of these three cyclic six-member ring species are experimentally found to increase with the temperature which then then hit peak around 1400 K and then subsequently decrease. Our model predicts such trends quite well although it underestimates concentration of cyclohexene and ethylidenecyclohexane. Attempts to improve the agreement between experiment and simulation for all the species were not successful. The overall agreement between experiment and simulation for most of the important products indicate that the model works reasonably well for pyrolysis of IPCH in the T and P range of this study.

3.3.4.3 Rate-of-production (ROP) and sensitivity analysis

Reaction flux analysis and sensitivity analysis have been performed to understand the important pathways of IPCH consumption, the various dissociation pathways of unstable radicals and formations of aromatic products. We discuss these in detail in this section.

Consumption of IPCH

Figure 3.34 shows the reaction flux of IPCH at 1282 K revealing the main pathways of IPCH consumption. It can be seen that IPCH is mostly consumed by unimolecular dissociation reactions as well as H-abstraction reactions by H atom and CH_3 radical. The H-abstraction reaction has the most important contribution with the dominant route being the formation of secondary radical, S3XIPCH (i.e., 21%).

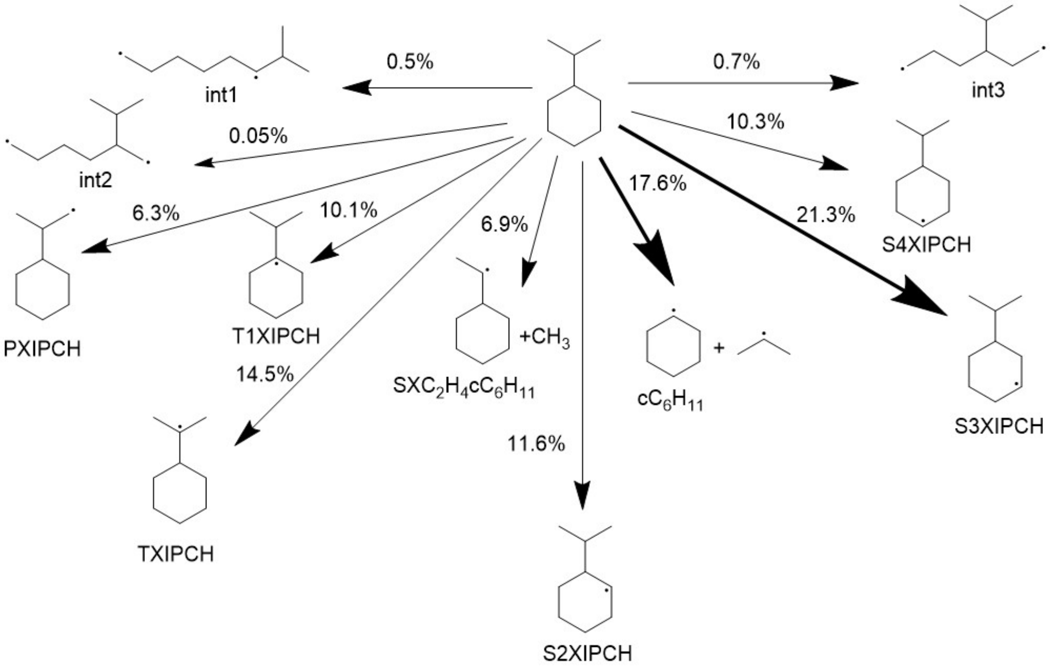

Figure 3.34: Reaction pathways consuming IPCH at 1282 K temperature with approximately 60% IPCH conversion. The number above the arrow indicates the respective percentage contribution to the overall contribution.

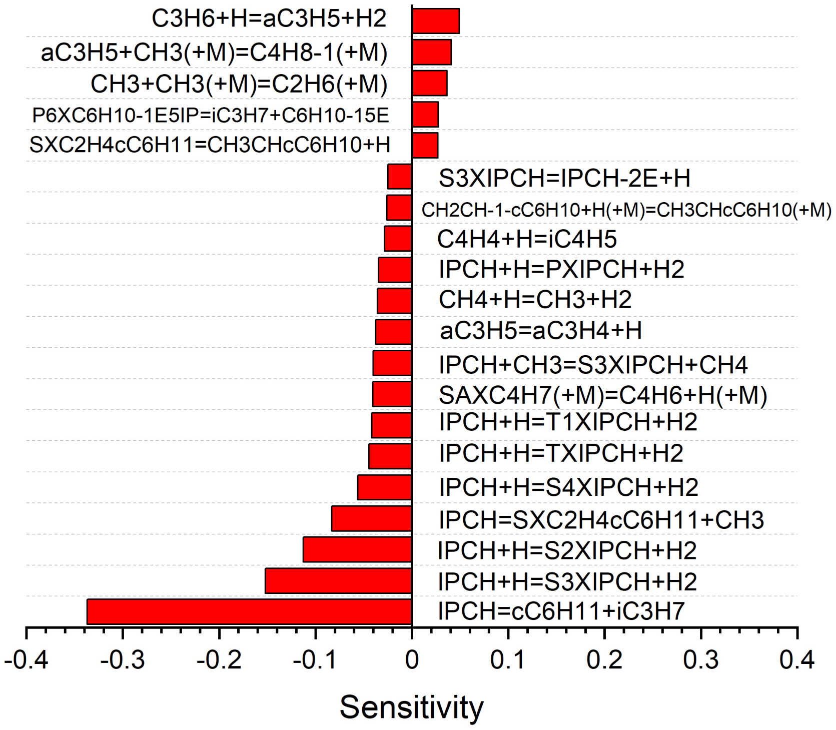

Figure 3.35: Normalized sensitivity analysis of IPCH at 1282K temperature with approximately 60% IPCH conversion. Only the top 20 sensitive reactions have been shown.

Among unimolecular dissociation reactions C_3H_7 elimination reaction has been found to be the dominant route (i.e., 17.6% contribution). The ring opening isomerization process has very minor role in IPCH consumption and had only 1.2% overall contribution. Thus, we can see that H-abstraction on both iso-propyl group as well as on cyclohexane ring are important in IPCH consumption. To further clarify the effect of unimolecular decomposition and H- atom abstraction reactions on IPCH consumption, the sensitivity analysis of IPCH has been done at 1282K (figure 3.35 shows the sensitivity analysis). The most sensitive reaction has been the dissociation of IPCH to isopropyl radical and cyclohexyl radical (C_3H_7 elimination channel) followed by the abstraction reaction to form S3XIPCH. The positive effects of these reactions on IPCH consumption occurred because these are the direct consumption channels of IPCH. H-atom abstraction reactions of IPCH are rapid when more H atom/CH_3 radical are added into the system. This is evident from the positive effect of H-elimination reaction from butenyl ($SAXC_4H_7$), allyl (aC_3H_5) and other radicals and negative effect of H/CH_3 abstraction by CH_3, C_3H_5 radical, C_3H_6 etc. on IPCH consumption.

Decomposition of alkylcyclohexyl radicals

From initial consumption process of IPCH, eight different alkylcyclohexane radicals are formed, namely PXIPCH (primary radical), cC_6H_{11}, $SXC_2H_4cC_6H_{11}$, S2XIPCH, S3XIPCH, S4XIPCH (secondary radicals), TXIPCH and T1XIPCH (tertiary radicals).

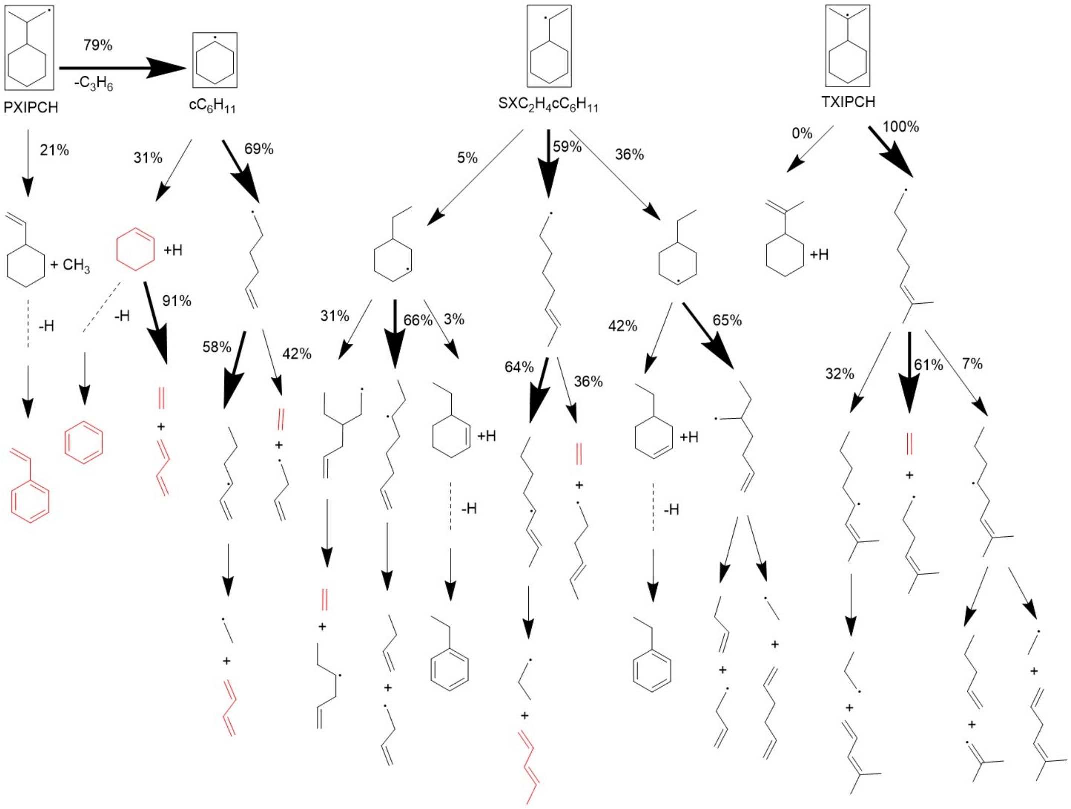

Figure 3.36: Reaction flux analysis of PXIPCH, cC_6H_{11}, $SXC_2H_4cC_6H_{11}$, and TXIPCH at 1282K. Species labelled with red have been detected in our experiment. The number above the arrow indicates the percentage contribution to the overall contribution.

To understand the detailed processes of the pyrolysis of IPCH, reaction flux analysis of major intermediates (radicals) that are formed after initial decomposition of IPCH have been performed at 1282 K. Figure 3.36 gives a summary of the consumption of PXIPCH, cC6H11, $SXC_2H_4cC_6H_{11}$ and TXIPCH at 1282 K.

PXIPCH is mainly converted (79%) to cC_6H_{11} by C_3H_6 elimination whereas H elimination to form ethylenecyclohexane has less contribution (21%). Ethenylcyclohexane can form styrene by step-wise dehydrogenation process. For cC_6H_{11}, ring opening process occurs predominantly (69%) leading to hexene radicals. H elimination from cC_6H_{11} to form cyclohexene also has significant contribution (31%). For $SXC_2H_4cC_6H_{11}$ and T1XIPCH, ring opening process forming alkenyl radical is the major decomposition channel. Alkenyl radicals formed from those process either undergo direct $\beta-C-C$ dissociation or isomerization (intermolecular 1,4-H shift) followed by $\beta-C-C$.

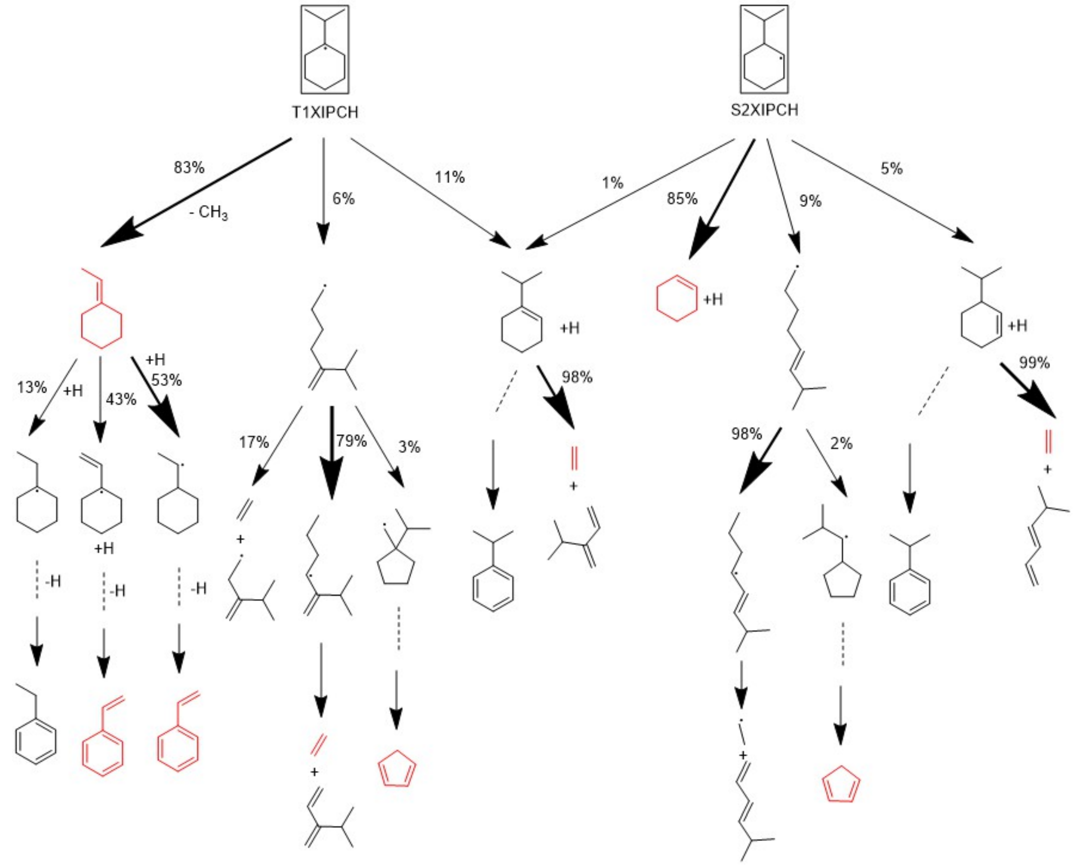

Figure 3.37: Reaction flux analysis of T1XIPCH, and S2XIPCH at 1282 K. Species labelled with red have been detected in our experiment. The number above the arrow indicates the percentage contribution to the overall contribution.

Similar trend is also observed for T1XIPCH, S2XIPCH (Figure 3.37) and S3XIPCH, S4XIPCH (Figure 3.38).

Cyclopentane radical can also be formed by isomerization of alkenyl radicals but has only minor contribution. This radical leads to cyclopentadiene by subsequent

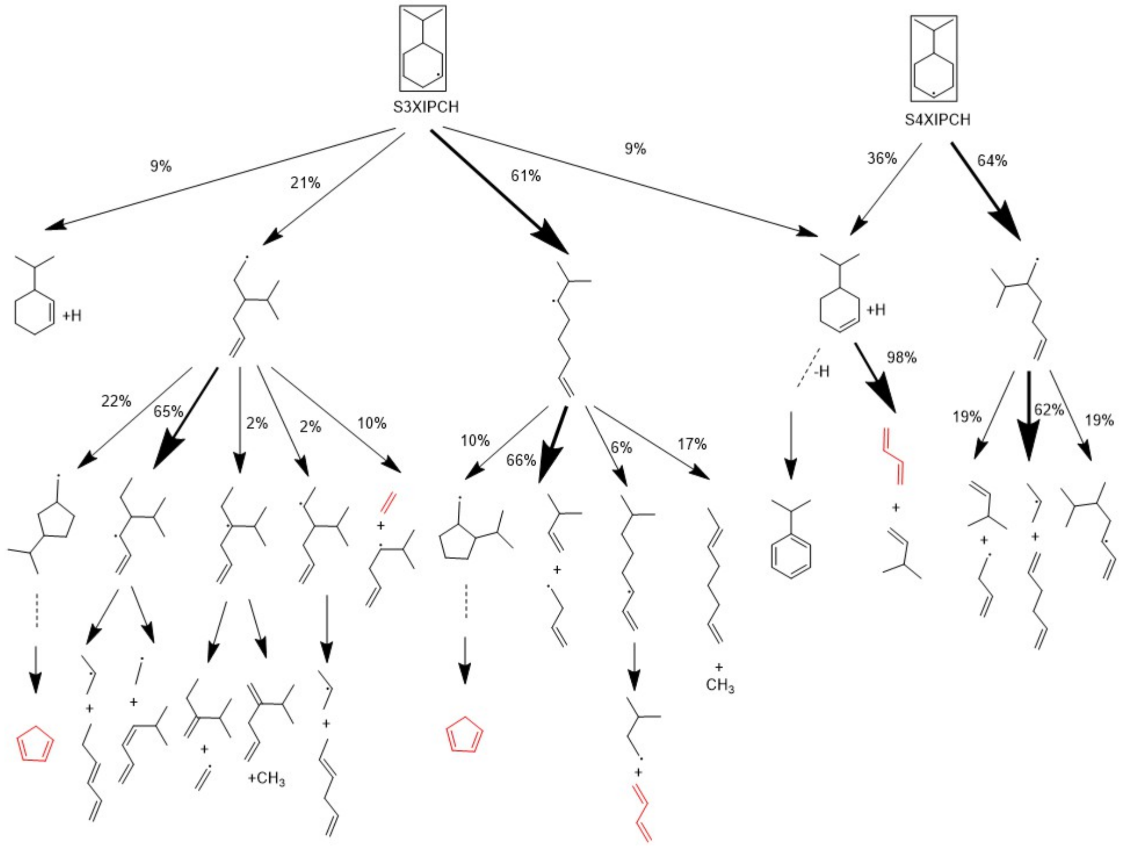

Figure 3.38: Reaction flux analysis of S3XIPCH, and S4XIPCH at 1282 K. Species labelled with red have been detected in our experiment. The number above the arrow indicates the percentage contribution to the overall contribution.

isomerization and stepwise dehydrogenation/dealkylation processes. Cyclohexene is also formed from cyclohexyl radicals (cC_6H_{11}). It can either dissociate (reverse Diels-Alder reaction) to alkene and diene or undergo stepwise dehydrogenation to form aromatic intermediate.

In summary, the ring-opening isomerization of cyclohexyl radical and alkylcyclohexane radicals form various alkenyl radicals. They lead to diene of methylhexadiene (5-methyl-1,6-hexadiene etc.), hexadiene (1,3-hexadiene, 1,4-hexadiene etc.), methylpentadiene (4-methyl-1,3-pemtadiene), pentadiene(1,3-pentadiene), alkylbutadiene (2-isopropyl-1,3-butadiene), 1,3-butadiene and cyclopentadiene; ethene, propene, butene; radicals of CH_3, C_2H_5, C_3H_7, C_4H_9 etc. Dehydrogenation/dealkylation of cyclohexyl radical and alkylcyclohexane radicals forms cyclohexene and various alkylcyclohexene respectively. They lead to diene of methylhexadiene (5-methyl-1,6-hexadiene), alkyllbutadiene (2-isopropyl-1,3butadiene), 1,3-butadiene; alkene of methylbutene (3-methylbutene), C_2H_4; and aromatic intermediate (benzene, styrene etc).

Reaction pathway analysis for benzene, toluene, and styrene formations

Figure 3.39 shows the reaction pathways analysis of benzene with IPCH conversion of approximately 85% at 1414 K.

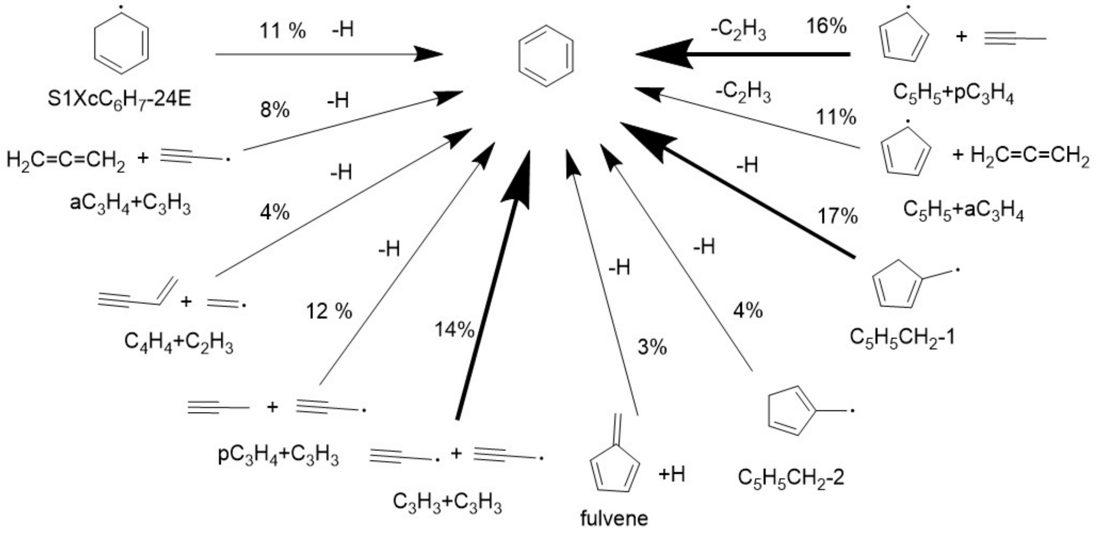

Figure 3.39: Reaction pathways analysis for formation of benzene in IPCH pyrolysis at 1414 K with IPCH conversion of approximately 85%.

Benzene is produced from multiple channels in IPCH pyrolysis. Methylcyclopendadiene radical (primary radical) has an important role in benzene formation with the dominant channel (17%) being benzene formation from primary radical of 1-methylcyclopentadiene radical (C5H5CH2-1). Benzene is also formed from primary radical of 2-methylcyclopentadiene (C5H5CH2-2). Cyclopentadiene radical leads to benzene by reaction either with propyne (16%) or with allene (11%). Formation of benzene by isomerization of fulvene has little contribution (3%). H-loss of cyclohexadienyl ($S1XcC_6H_7-24E$) radical is one of the important benzene formation route. Stepwise dehydrogenation/ dealkylation of cyclohexyl (cC_6H_{11}) radical, and alkylcyclohexane (PXIPCH, S3XIPCH and S3XIPCH) radicals are the source of cyclohexadienyl radical. Other important reactions accounting for benzene formation are the resonance stabilized radicals:
$C_3H_3 + C_3H_3$ (14%),
$pC_3H_4 + C_3H_3$(12%),
$aC_3H_4 + C_3H_3$ (8%)
and $C_4H_4 + C_2H_3$ (4%).

The sensitivity analysis for benzene is shown in figure 3.40.

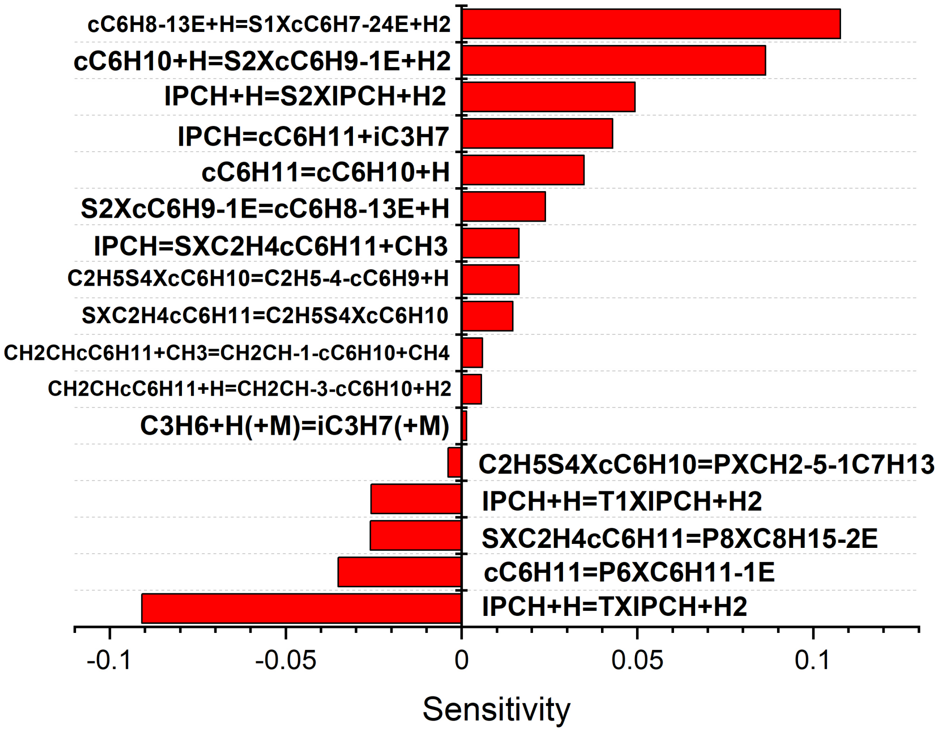

Figure 3.40: Normalized sensitivity analysis of benzene at 1414 K temperature with approximately 85% IPCH conversion.

Formation of cyclohexadienyl ($S1XcC_6H_7 - 24E$) radical is found to be the most sensitive reaction and has the positive effect on benzene formation. Cyclohexyl radical (cC_6H_{11}) also has significant effect on benzene formation. For example, formation of cC_6H_{11} ($IPCH = cC_6H_{11} + iC_3H_7$) and the $\beta - C - H$ scission of cC_6H_{11} ($cC_6H_{11} = cC_6H_{10} + H$) had positive effects on benzene formation, while its isomerization via ring-opening ($cC_6H_{11} = P6XC_6H_{11} - 1E$) had the 2nd most negative effect on benzene formation. TXIPCH and T1XIPCH formation had negative effect on benzene formation as these radicals prefer to open its ring rather than forming cyclohexene. Formation of S2XIPCH had a positive effect on benzene formation as it prefers to form cC_6H_{10} via C_3H_7 elimination. Overall, ring-opening of cyclohexyl radical had negative effect on benzene formation and dehydrogenation/dealkylation of these radicals have positive effect on benzene formation.

Figure 3.41 shows the reaction pathway of toluene and styrene formations with IPCH conversion of approximately 85% at 1414 K.

The dominant source of toluene is the association of H-atom with primary toluene radical ($A1CH_2$) from the various H atom sources (H atom (30%), C_3H_6(34%), C_5H_6 (3%), pC_3H_4 (4%), and C_2H_4 (2%)). Other important reaction for toluene formation is that of the addition of resonance stabilized radicals, such as reaction of propargyl radical with vinylacetylene ($C_3H_3 + C_4H_4$) (25%).

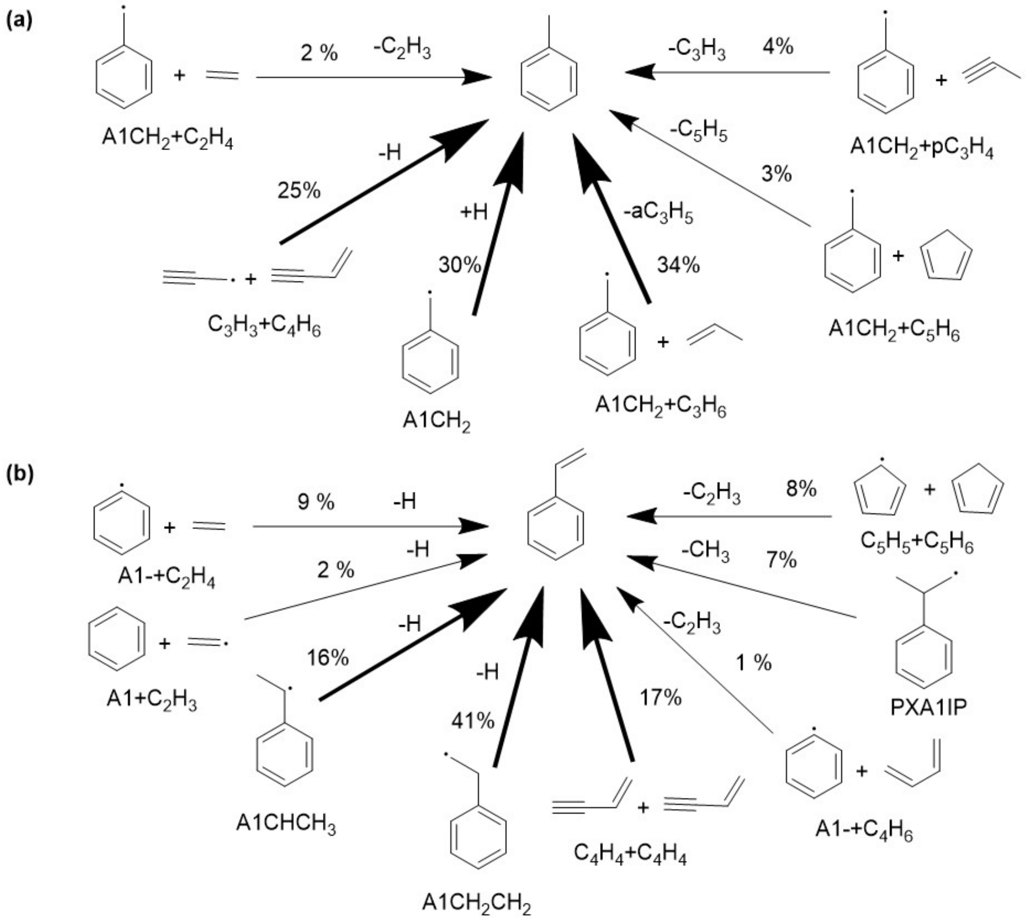

Figure 3.41: Reaction pathways analysis for formation of (a) toluene and (b) styrene in IPCH pyrolysis at 1414 K with IPCH conversion of approximately 85%.

Styrene is produced from multiple channels. The dominant channel of styrene formation is the H-atom elimination from ethylbenzene radical. Elimination from primary ethylbenzene radical (A1CH2CH2) has major contribution (41%), in forming styrene followed by that of secondary radical ($A1CHCH_3$) (16%). Iso-propylbenzene radical (PXA1IP) also leads to styrene by H-atom elimination (7%). As shown in previous section, ethylbenzene is formed by stepwise dehydrogenisation of SXC_2H_4 $cC6H_{11}$ and T1XIPCH and iso-propylbenzene formed by stepwise dehydrogenisation of T1XIPCH, S2XIPCH, S3XIPCH and S4XIPCH. Styrene is also formed by the reaction between benzyl radical and C_2H_4 (9%), benzene and C_2H_3 radical (2%), and also benzyl radical with 1,3-butadiene (1%). Cyclopentadiene reacts with cyclopentadienyl radical leads to give styrene and it has a significant contribution (8%). Addition reaction between two vinylacetylene (C_4H_4) also forms styrene and is found to be the 2nd most dominant channel of the formation of styrene (17%).

Figure 3.42 corresponding to the sensitivity analysis for toluene and styrene.

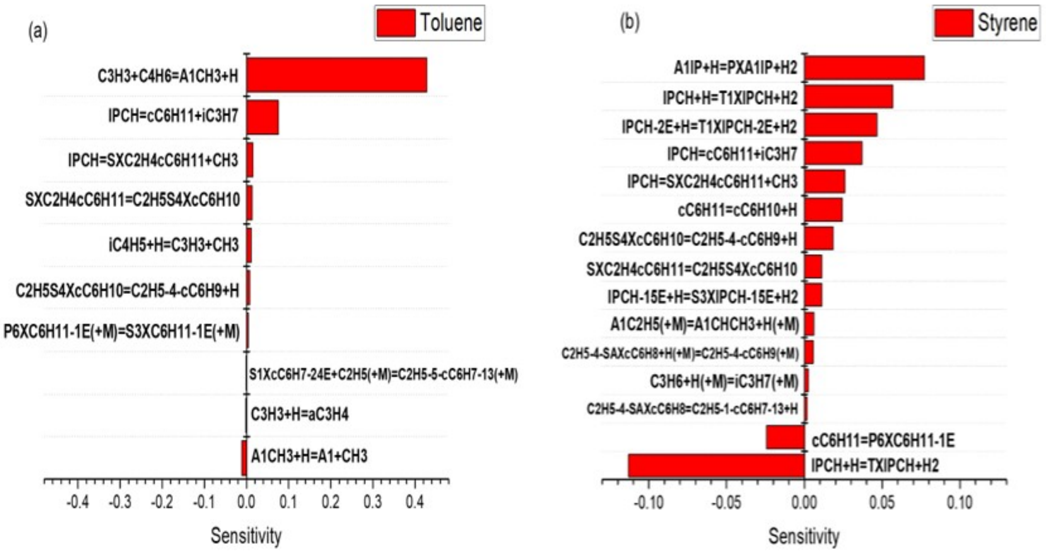

Figure 3.42: Normalized sensitivity analysis of (a) toluene and (b) styrene at 1414 K temperature with approximately 85% IPCH conversion.

Addition reaction of propargyl radical (C_3H_3) and 1,3-butadienne (C_4H_6) is found to be the most sensitive reaction which has positive effect on toluene formation. Formation of benzene by the reaction of toluene with H-atom ($A1CH_3 + H = A1 + CH_3$) had the most negative effect on toluene formation. cC_6H_{11} also plays an important role, the formation of which has positive effect on toluene formation.

As for styrene formation, H-abstraction of IPCH leading to TXIPCH radical is found to be the most sensitive reaction for styrene formation and has the negative effect on it. This is due to the fact that TXIPCH prefer to isomerization via ring-opening rather than forming cyclohexane by H-elimination. Formation of PXA1IP has the most positive effect on the styrene formation, since PXA1IP easily leads to styrene by H-elimination. Similarly, formation of PXIPCH also has the positive effect on styrene formation as it leads to ethenylcyclohexane by CH_3 elimination. Ethenylcyclohexane can further form styrene by stepwise dehydrogenation. Like in the case of benzene and toluene formation, cC_6H_{11} also plays a critical role in styrene formation, and the $\beta - C - H$ scission of cC_6H_{11} ($cC_6H_{11} = cC_6H_{10}+H$) has the positive effect on styrene formation, whereas its isomerization via ring-opening ($cC_6H_{11} = P6XC_6H_{11} - 1E$) negatively affect styrene formation.

In summary, cC_6H_{11} plays a critical role in the formation of all aromatic products and its $\beta - C - H$ scission process ($cC_6H_{11} = cC_6H_10 + H$) has the positive effect on aromatics formation, while its isomerization via ring-opening ($cC_6H_{11} = P6XC_6H_{11} - 1E$) had the negative effect on aromatics formation. Other IPCH radicals also affect aromatics formation wherein the direct dehydrogenation/ dealkylation of these radicals has positive effects while their isomerization via ring-opening has negative effects. Apart from various cyclohexyl radicals, various resonance stabilized radicals also contribute to formation of aromatic products.

3.3.5 Rate constant of overall decomposition of IPCH

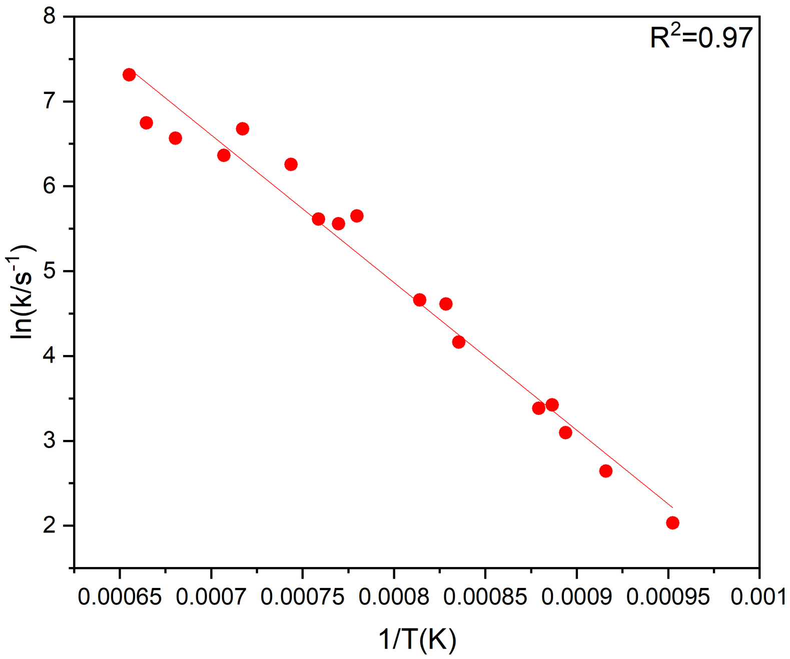

Figure 3.43: Arrhenius plot of overall decomposition of IPCH.

The overall rate coefficient for the thermal decomposition of IPCH in the temperature range between 1050 K and 1526 K has been determined using the following equation:

$$k = -\frac{1}{t} \ln \frac{[IPCH]_t}{[IPCH]_0} \tag{3.2}$$

Here t is the reaction time (dwell time), $[IPCH]_0$ is the initial concentration of IPCH and $[IPCH]_t$ is the concentration of IPCH after time t.

The rate constant expression which was obtained by linear fitting the data in figure 3.43:

$$k/s^{-1} = 10^{8.16 \pm 0.25} \exp^{\frac{(-34.6 \pm 1.5/kcal.mol^{-1})}{RT}} \tag{3.3}$$

3.4 Conclusion

In the present chapter, we investigated thermal decomposition/pyrolysis of IPCH both theoritically and experimentally.

Thoeoritcal study shows the following conlusion:
i)The pyrolysis mechanism of IPCH includes
unimolecular decomposition and isomerization,
H-atom abstraction,
dissociation of alkene and alkylcyclohexene,
decomposition and isomerization of alkylcyclohexane radicals,
decomposition and isomerization of alkenyl radicals, and
stepwise dehydrogenation of cyclic intermediate.

ii)The initial step of thermal decomposition of IPCH is the C-C bond decomposition channel instead of ring-opening isomerization channel. The iso-propyl group in cyclohexane makes the C-C dissociation barrier lase than that for the C-C bond in methylcyclohexane.

iii)H-abstraction reaction barrier for IPCH is higher than H-abstraction reaction in methyl-cyclohexane (although the energy difference is within 0.5 kcal/mol).

iv)For ring-opening isomerization of IPCH radical, C-C bond dissociation adjacent to the iso-propyl group has a lower energy barrier than the other IPCH radical, which is a similar trend for MCH radical and ECH radical as well. Although energy barrier of ring-opening is less for IPCH radical compared to that of MCH radical and ECH radical. The lowest energy pathway among IPCH radicals was the dissociation via $\beta - C - C$ scission (C_3H_6 elimination).

v)Alkenyl radicals are obtained by opening the ring of IPCH radical. These alkenyl radicals then either isomerize to cyclopentane radical (energetically most favorable) or isomerized to other alkenyl radicals by intramolecular H-migration or dissociate via β-scission.

vi)Cyclopentadiene, methylcyclopentadiene, benzene, and styrene are formed by stepwise dehydrogenation of cyclic intermediates. Stepwise dehydrogenation of iso-propylcyclohexene are energetically favorable than that of similar stepwise dehydrogenation of cyclohexene. Small hydrocarbons like methane, ethylene, propylene, butadiene, pentadiene etc., are also formed as a final product of IPCH.

Experimentally we have investigated the pyrolysis of IPCH by measuring species distribution in the post shocked mixture inside the shock tube for the temperature range of 923-1526 K and pressure ranging from 9.8–20.2 bar. A kinetic model for IPCH has been built which includes 426 species and 1354 reactions. The kinetic model has been validated against our experimental data. In general, the kinetic model gives good predictions agreeing reasonably well with the experimental data. Methane, ethene, acetylene, ethane, propene, allene, propyne, vinylacetylene, 1,3-butadiene, pentadiene, cyclopentadiene, and benzene are the major products of pyrolysis observed in the current study. Ethene is the most abundant product at high temperature followed by acetylene. Benzene is the most abundant aromatic product followed by toluene and styrene which are present in little amount. IPCH starts dissociating around 1050 K. ROP study reveals that C_3H_7 elimination reaction channel has strong effect on the unimolecular dissociation of IPCH and it is the most sensitive reaction for IPCH consumption. Apart from C_3H_7 and CH_3 elimination decomposition channels of IPCH, the contributions of the H-abstraction reactions of IPCH on its consumption are also significant. Presence of iso-propyl group on the cyclohexene ring makes IPCH to produce branched unsaturated species like, methylpentadiene, methylbutadiene, and methylcyclopentadiene. Another feature of IPCH pyrolysis is that it can easily produce cyclohexyl radical (cC_6H_{11}) that can lead to the formation of cyclohexene and cyclohexadiene. ROP analysis of the formation of the aromatic products reveals that stepwise dehydrogenation/ dealkylation of cyclic intermediates (cyclopentadiene radical, cyclohexadiene radical etc.), as well as addition of resonance stabilized radical/intermediates (C_3H_3, aC_4H_4, pC_3H_4, C_4H_6 etc) have significant contributions on the formations of the benzene, toluene and styrene. Sensitivity analyses illustrate that cC_6H_{11} plays a key role in the formation of aromatic products (benzene, toluene, and styrene) and its $\beta - C - H$ scission process ($cC_6H_{11} = cC_6H_{10} + H$) has the positive effect on aromatics formation, while its isomerization via ring-opening ($cC_6H_{11} = P6XC_6H_{11} - 1E$) has the negative effect on aromatic formation. Other IPCH radicals also affect aromatics formation, and following the same trend as that of cC_6H_{11}, (i.e. the direct dehydrogenation/ dealkylation of these radicals have positive effects while their isomerization via ring-opening have negative effects).

Overall, presence of iso-propyl group in cyclohexene ring, makes it easy to the formation of aromatic during pyrolysis. The rate of overall decomposition of IPCH has been calculated and expressed in the equation 3.3.

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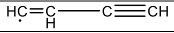
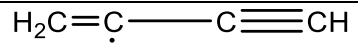
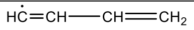
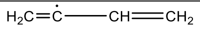
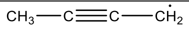
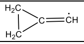
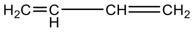
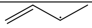
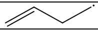
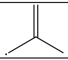
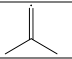
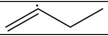
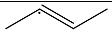
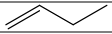
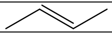
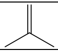
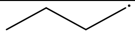
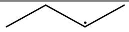
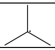
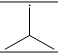
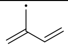
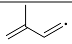
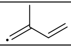
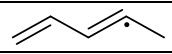
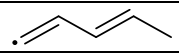
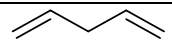
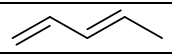
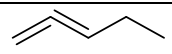
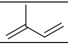
3.5 Additional Information

3.5.1 Nomenclature and structure of the species in the mechanism

formula	nomenclature	structure	formula	nomenclature	structure
C_4H	C4H	$HC\equiv C-C\equiv C\cdot$	C_4H_2	C4H2	$HC\equiv C-C\equiv CH$
C_4H_3	nC4H3	 $H\underset{\cdot}{C}=\underset{H}{C}-C\equiv CH$	C_4H_3	iC4H3	 $H_2C=\underset{\cdot}{C}-C\equiv CH$
C_4H_4	C4H4	$H_2C=CH-C\equiv CH$	C_4H_5	nC4H5	 $H\dot{C}=CH-CH=CH_2$
C_4H_5	iC4H5	 $H_2C=\dot{C}-CH=CH_2$	C_4H_5	C4H5-2	 $CH_3-C\equiv C-\dot{C}H_2$
C_4H_5	c-C4H5		C_4H_6	C4H6	 $H_2C=\underset{H}{C}-CH=CH_2$
C_4H_6	C4H612	$H_2C=C=CH-CH_3$	C_4H_6	C4H6-2	$CH_3-C\equiv C-CH_3$
C_4H_7	SAXC4H7		C_4H_7	C4H7	
C_4H_7	iC4H7		C_4H_7	iC4H7-1	
C_4H_7	C4H7-2		C_4H_7	CH3CCHCH3	
C_4H_8	C4H8-1		C_4H_8	C4H8-2	
C_4H_8	iC4H8		C_4H_9	pC4H9	
C_4H_9	sC4H9		C_4H_9	tC4H9	
C_4H_9	iC4H9		C_5H_7	P1XCH2C4H5-13E	
C_5H_7	S4XC4H4-13E2M		C_5H_7	S1XC4H4-13E2M	
C_5H_7	T4XC5H7-13E		C_5H_7	T1XC5H7-13E	
C_5H_8	C5H8-14E		C_5H_8	C5H8-13E	
C_5H_8	C5H8-12E		C_5H_8	C4H5-13E2M	
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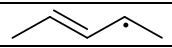
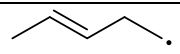
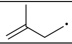
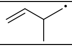
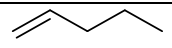
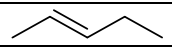
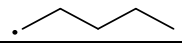
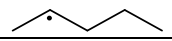
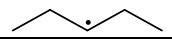
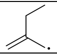
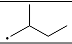
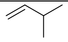
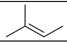
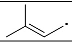
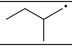
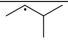
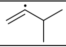
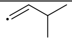
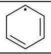
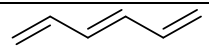
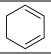
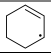
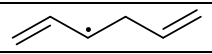
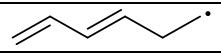
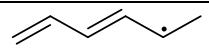
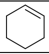
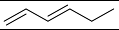
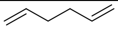
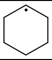
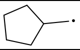
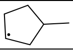
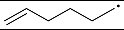
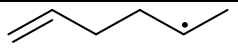
C_5H_9	S4XC5H9-1E		C_5H_9	S4XC5H9-2E	
C_5H_9	P5XC5H9-2E		C_5H_9	P4XC4H6-1E2M	
C_5H_9	P4XC4H6-1E3M		C_5H_{10}	C5H10-1E	
C_5H_{10}	C5H10-2E		C_5H_{11}	P1XC5H11	
C_5H_{10}	S2XC5H11		C_5H_{11}	S3XC5H11	
C_5H_7	cC5H7		C_5H_9	PAXCH2-2-1C4H7	
C_5H_{11}	P1XC4H82M		C_5H_{10}	C4H7-1E3M	
C_5H_{10}	C4H7-2E2M		C_5H_9	P4XC4H6-2E2M	
C_5H_{11}	P4XC4H83M		C_5H_{11}	S2XC4H83M	
C_5H_9	T2XC4H6-1E3M		C_5H_9	S1XC4H6-1E3M	
C_6H_7	S1XcC6H7-24E		C_6H_8	C6H8-135E	
C_6H_8	cC6H8-13E		C_6H_9	S2XcC6H9-1E	
C_6H_9	S3XC6H9-15E		C_6H_9	P6XC6H9-13E	
C_6H_9	S5XC6H9-13E		C_6H_{10}	cC6H10	

			C_6H_{10}	C6H10-13E	
C_6H_{10}	C6H10-15E		C_6H_{11}	cC6H11	
C_6H_{11}	P1XCH2cC5H9		C_6H_{11}	S3XcC5H81M	
C_6H_{11}	P6XC6H11-1E		C_6H_{11}	S5XC6H11-1E	
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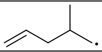
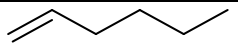
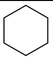
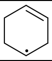
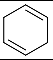
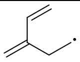
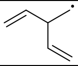
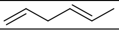
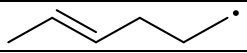
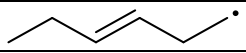
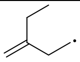
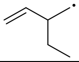
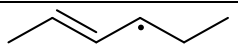
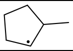
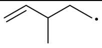
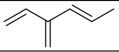
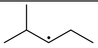
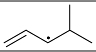
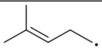
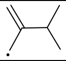
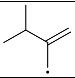
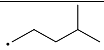
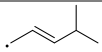
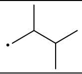
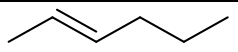
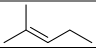
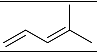
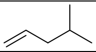
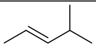
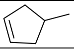
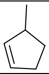
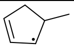
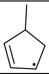
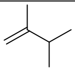
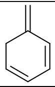
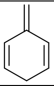
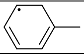
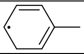
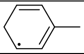
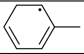
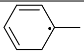
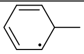
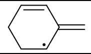
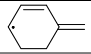
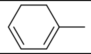
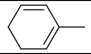
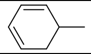
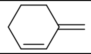
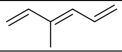
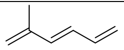
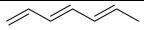
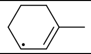
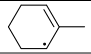
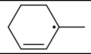
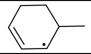
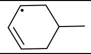
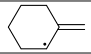
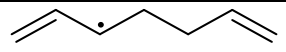
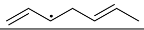
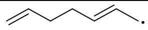
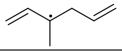
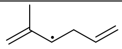
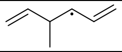
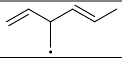
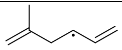
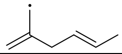
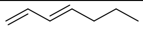
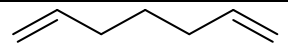
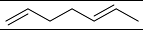
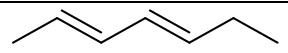
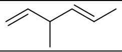
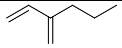
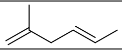
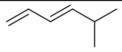
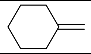
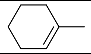
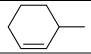
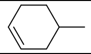
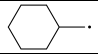
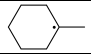
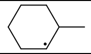
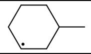
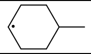
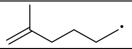
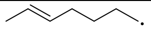
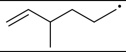
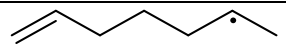
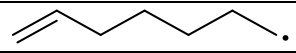
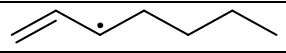
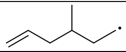
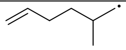
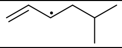
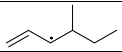
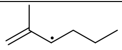
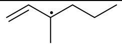
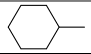
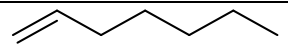
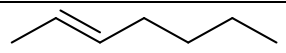
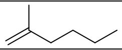
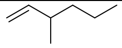
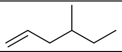
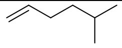
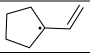
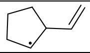
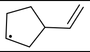
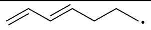
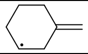
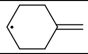
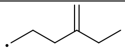
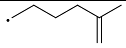
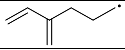
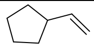
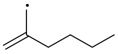
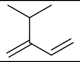
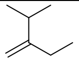
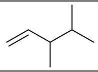
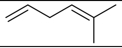
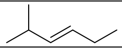
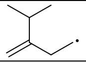
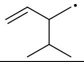
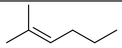
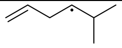
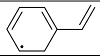
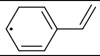
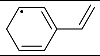
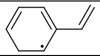
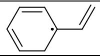
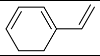
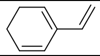
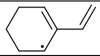
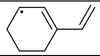
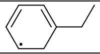
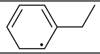
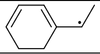
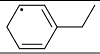
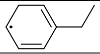
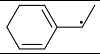
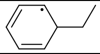
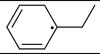
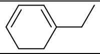
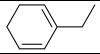
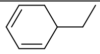
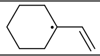
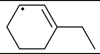
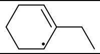
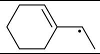
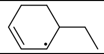
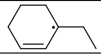
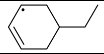
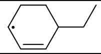
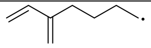
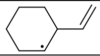
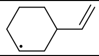
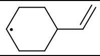
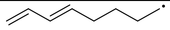
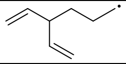
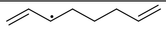
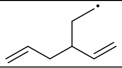
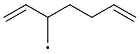
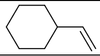
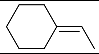
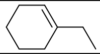
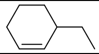
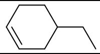
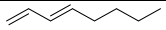
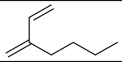
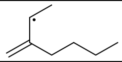
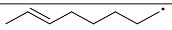
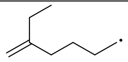
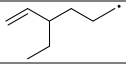
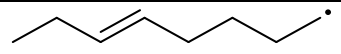
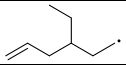
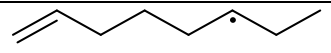
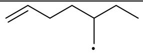
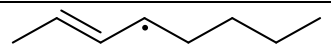
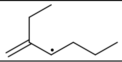
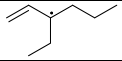
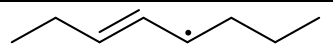
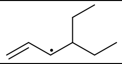
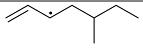
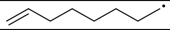
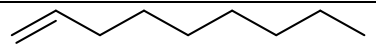
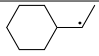
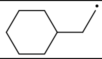
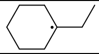
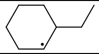
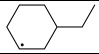
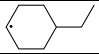
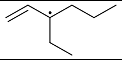
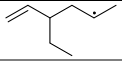
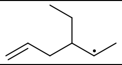
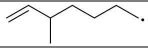
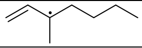
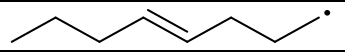
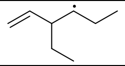
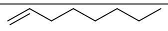
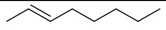
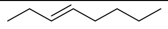
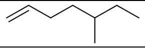
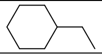
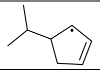
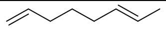
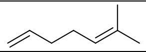
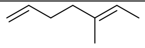
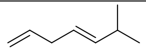
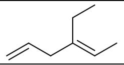
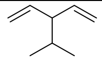
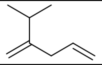
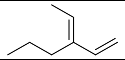
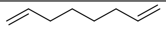
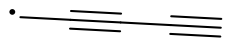
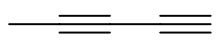
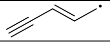
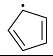
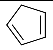
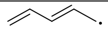
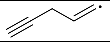
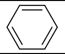
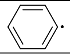
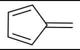
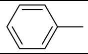
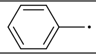
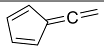
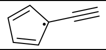
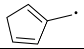
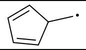
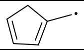
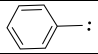
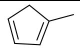
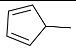
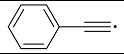
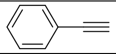
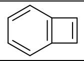
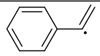
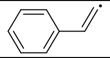
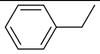
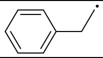
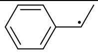
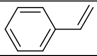
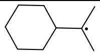
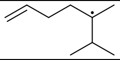
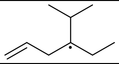
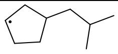
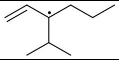
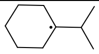
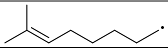
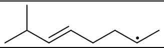
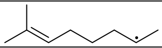
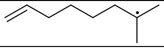
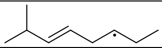
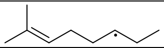
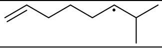
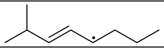
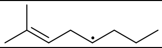
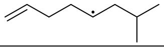
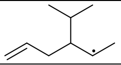
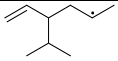
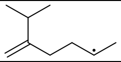
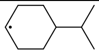
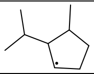
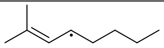
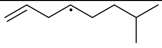
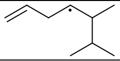
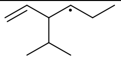
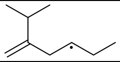
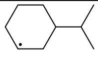
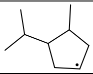
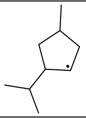
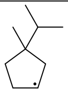
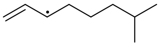
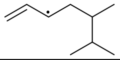
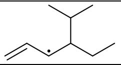
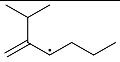
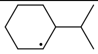
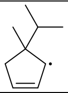
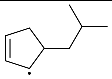
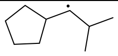
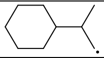
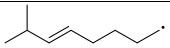
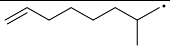
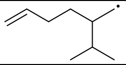
C_6H_{11}	P5XC5H8-1E4M		C_6H_{12}	C6H12-1E	
C_6H_{12}	cC6H12		C_6H_9	S3XcC6H9-1E	
C_6H_8	cC6H8-14E				
C_6H_9	C2H3-2-PXC4H6		C_6H_9	C2H3-3-PXC4H6	
			C_6H_{10}	C6H10-14E	
C_6H_{11}	P6XC6H11-2E		C_6H_{11}	P6XC6H11-3E	
C_6H_{11}	PXC2H4-2-1C4H7		C_6H_{11}	PXCH2-3-1C5H9	
C_6H_{11}	S4XC6H11-2E		C_6H_{11}	CH3S2XcC5H8	
C_6H_{11}	P5XC5H8-1E3M		C_7H_{10}	CH2-3-C6H8-14	
C_6H_{13}	S3XC5H102M		C_6H_{11}	S3XC5H8-1E4M	
C_6H_{11}	P5XC5H8-2E2M		C_6H_{11}	P3XC3H4-1E2IP	
C_6H_{11}	P1XCH2C4H6-1E3M		C_6H_{13}	P1XC5H104M	
C_6H_{11}	P1XC5H8-2E4M		C_6H_{13}	P1XC4H723M	
C_6H_{12}	C6H12-2E		C_6H_{12}	C5H9-2E2M	
C_6H_{10}	C5H7-13E4M		C_6H_{12}	**C5H9-1E4M**	
C_6H_{12}	C5H9-2E4M		C_6H_{10}	cC5H74M	
C_6H_{10}	cC5H75M		C_6H_9	S3XcC5H64M	
C_6H_9	S3XcC5H65M		C_6H_{12}	C4H6-1E23M	
C_7H_8	CH2cC6H6-13E		C_7H_8	CH2cC6H6-25E	
C_7H_9	S5XMCH-13E		C_7H_9	S4XMCH-15E	
C_7H_9	S3XMCH-15E		C_7H_9	S6XMCH-13E	
C_7H_9	T1XMCH-35E		C_7H_9	S2XMCH-35E	

C_7H_9	CH2S2XcC6H7-5E		C_7H_9	CH2S4XcC6H7-5E	
C_7H_{10}	MCH-13E		C_7H_{10}	MCH-15E	
C_7H_{10}	MCH-35E		C_7H_{10}	CH2cC6H8-2E	
C_7H_{10}	C6H7-135E3M		C_7H_{10}	C6H7-135E2M	
C_7H_{10}	C7H10-135E		C_7H_{11}	S3XMCH-1E	
C_7H_{11}	S2XMCH-6E		C_7H_{11}	T1XMCH-2E	
C_7H_{11}	S2XMCH-3E		C_7H_{11}	S5XMCH-3E	
C_7H_{11}	CH2S2XcC6H9		C_7H_{11}	S3XC7H11-16E	
C_7H_{11}	S3XC7H11-15E		C_7H_{11}	S4XC7H11-15E	
C_7H_{11}	S7XC7H11-15E		C_7H_{11}	T3XC6H8-15E3M	
C_7H_{11}	S3XC6H8-15E2M		C_7H_{11}	S4XC6H8-15E3M	
C_7H_{11}	P1XCH2-3C6H9-15E		C_7H_{11}	S4XC6H8-15E2M	
C_7H_{11}	P1XCH2C6H9-15E		C_7H_{12}	C7H12-13E	
C_7H_{12}	C7H12-16E		C_7H_{12}	C7H12-15E	
C_7H_{12}	C7H12-24E		C_7H_{12}	C6H9-15E3M	
C_7H_{12}	CH2-3-C6H10-1E		C_7H_{12}	C6H9-15E2M	
C_7H_{12}	C6H9-13E5M		C_7H_{12}	CH2cC6H10	
C_7H_{12}	MCH-1E		C_7H_{12}	MCH-2E	
C_7H_{12}	MCH-3E		C_7H_{13}	PXCH2cC6H11	
C_7H_{13}	T1XMCH		C_7H_{13}	S2XMCH	
C_7H_{13}	S3XMCH		C_7H_{13}	S4XMCH	
C_7H_{13}	P6XC6H10-1E2M		C_7H_{13}	P7XC7H13-2E	
C_7H_{13}	P6XC6H10-1E3M		C_7H_{13}	S6XC7H13-1E	
C_7H_{13}	P7XC7H13-1E		C_7H_{13}	S3XC7H13-1E	
C_7H_{13}	P6XC6H10-1E4M		C_7H_{13}	P6XC6H10-1E5M	
C_7H_{13}	S3XC6H10-1E5M		C_7H_{13}	S4XC7H13-2E	
C_7H_{13}	S3XC6H10-1E4M		C_7H_{13}	S3XC6H10-1E2M	
C_7H_{13}	T3XC6H10-1E3M		C_7H_{14}	MCH	
C_7H_{14}	C7H14-1E		C_7H_{14}	C7H14-2E	

C_7H_{14}	C6H11-1E2M		C_7H_{14}	C6H11-1E3M	
C_7H_{14}	C6H11-1E4M		C_7H_{14}	C6H11-1E5M	
C_7H_{11}	C2H3TXcC5H8		C_7H_{11}	C2H3S2XcC5H8	
C_7H_{11}	C2H3S3XcC5H8		C_7H_{11}	P7XC7H11-13E	
C_7H_{11}	CH2S3XcC6H9		C_7H_{11}	CH2S4XcC6H9	
C_7H_{11}	CH2-4-PXC6H9		C_7H_{11}	CH2-5-PXC6H9	
C_7H_{11}	C2H3-2-PXC5H8		C_7H_{12}	C2H3cC5H9	
C_7H_{13}	PAXCH2-2-1C6H11		C_7H_{12}	C4H5-13E2IP	
C_7H_{14}	C4H7-1E2IP		C_7H_{14}	C5H8-1E34M	
C_7H_{12}	C6H9-14E5M		C_7H_{14}	C6H11-3E2M	
			C_7H_{13}	P4XC4H6-1E2IP	
C_7H_{13}	P4XC4H6-1E3IP		C_7H_{13}	P6XC6H10-2E2M	
C_7H_{13}	S4XC6H10-1E5M		C_8H_9	CH2CH-1-SAXcC6H6	
C_8H_9	CH2CH-2-SAXcC6H6		C_8H_9	CH2CH-3-SAXcC6H6	
C_8H_9	CH2CH-4-SAXcC6H6		C_8H_9	CH2CH-5-SAXcC6H6	
C_8H_{10}	CH2CH-1-cC6H7-13		C_8H_{10}	CH2CH-2-cC6H7-13	
C_8H_{11}	CH2CH-2-SAXcC6H8		C_8H_{11}	CH2CH-1-SAXcC6H8	
C_8H_{11}	C2H5-1-SAXcC6H6		C_8H_{11}	C2H5-4-SAXcC6H6	
C_8H_{11}	CH3CH-1-cC6H7-13		C_8H_{11}	C2H5-3-SAXcC6H6	
C_8H_{11}	C2H5-2-SAXcC6H6		C_8H_{11}	CH3CH-2-cC6H7-13	
C_8H_{11}	C2H5-6-SAXcC6H6		C_8H_{11}	C2H5-5-SAXcC6H6	
C_8H_{12}	C2H5-1-cC6H7-13		C_8H_{12}	C2H5-2-cC6H7-13	
C_8H_{12}	C2H5-5-cC6H7-13		C_8H_{13}	CH2CH-1-cC6H10	
			C_8H_{13}	C2H5-1-SAXcC6H8	
C_8H_{13}	C2H5-2-SAXcC6H8		C_8H_{13}	CH3CH-1-cC6H9	

C_8H_{13}	C2H5-4-SAXcC6H8		C_8H_{13}	C2H5-3-SAXcC6H8	
C_8H_{13}	C2H5-5-SAXcC6H8		C_8H_{13}	C2H5-6-SAXcC6H8	
C_8H_{13}	C2H3-2-PXC6H10		C_8H_{13}	CH2CH-2-cC6H10	
C_8H_{13}	CH2CH-3-cC6H10		C_8H_{13}	CH2CH-4-cC6H10	
C_8H_{13}	PXC8H13-13		C_8H_{13}	C2H3-3-PXC6H10	
C_8H_{13}	SAXC8H13-17		C_8H_{13}	C2H3-4-PXC6H10	
C_8H_{13}	C2H3-5-PXC6H10		C_8H_{14}	CH2CHcC6H11	
C_8H_{14}	CH3CHcC6H10		C_8H_{14}	C2H5-1-cC6H9	
C_8H_{14}	C2H5-3-cC6H9		C_8H_{14}	C2H5-4-cC6H9	
C_8H_{14}	C8H14-13E		C_8H_{14}	C2H3-2-1C6H11	
C_8H_{15}	CH3CH-2-1C6H11		C_8H_{15}	P8XC8H15-2E	
C_8H_{15}	C2H5-2-PXC6H10		C_8H_{15}	C2H5-3-PXC6H10	
C_8H_{15}	P8XC8H15-3E		C_8H_{15}	PXC2H4-4-1C6H11	
C_8H_{15}	S6XC8H15-1E		C_8H_{15}	PXCH2-5-1C7H13	
C_8H_{15}	S4XC8H15-2E		C_8H_{15}	C2H5-2-SAX1C6H10	
C_8H_{15}	C2H5-3-TAX1C6H10		C_8H_{15}	S5XC8H15-3E	
C_8H_{15}	C2H5-4-SAX1C6H10		C_8H_{15}	S3XC7H12-1E5M	
C_8H_{15}	P8XC8H15-1E		C_8H_{15}	S3XC8H15-1E	
C_8H_{15}	SXC2H4cC6H11		C_8H_{15}	PXC2H4cC6H11	
C_8H_{15}	C2H5TXcC6H10		C_8H_{15}	C2H5S2XcC6H10	
C_8H_{15}	C2H5S3XcC6H10		C_8H_{15}	C2H5S4XcC6H10	
			C_8H_{15}	C3H7-3-SXC5H8	
			C_8H_{15}	C2H5-3-SXC6H10	
			C_8H_{15}	C2H5-4-SXC6H10	
C_8H_{15}	P7XC7H12-1E3M		C_8H_{15}	T3XC7H12-1E3M	
			C_8H_{15}	P8XC8H15-4E	

C_8H_{15}	C2H5-3-S2XC6H10				
C_8H_{16}	C8H16-1E		C_8H_{16}	C8H16-2E	
C_8H_{16}	C8H16-3E		C_8H_{16}	C7H13-1E5M	
			C_8H_{16}	C2H5cC6H11	
C_8H_{13}	S1XcC5H65IP		C_8H_{14}	C8H14-16E	
C_8H_{14}	C7H11-15E6M		C_8H_{14}	C7H11-15E5M	
C_8H_{14}	C7H11-14E6M		C_8H_{14}	C6H9-14E4Et	
C_8H_{14}	C5H7-14E3IP		C_8H_{14}	C5H7-14E2IP	
C_8H_{14}	C5H7-13E3C3H7		C_8H_{14}	C8H14-17E	
C_5H_3	C5H3		C_5H_4	cC5H4	
C_5H_4	C5H4		C_5H_5	lC5H5	
C_5H_5	C5H5		C_5H_6	C5H6	
C_5H_7	lC5H7		C_5H_5	C5H52	
			C_6H_6	A1	
C_6H_5	A1-				
C_6H_6	fulvene				
			C_7H_9	A1CH3	
C_7H_8	A1CH2		C_7H_6	C7H6	
C_7H_5	C7H5		C_6H_7	C5H5CH2-2	
C_6H_7	C5H5CH2-3		C_6H_7	C5H5CH2-1	
			C_7H_7	A1CH	
C_6H_8	cC5H5-13E1M		C_6H_8	cC5H5-13E5M	
C_8H_5	A1CC				
			C_8H_6	A1C2H	
C_8H_6	A1cC2H2		C_8H_7	A1CCH2	
C_8H_7	A1CHCH				

C_8H_{10}	A1C2H5		C_8H_9	A1CH2CH2	
C_8H_9	A1CHCH3		C_8H_8	A1C2H3	
C_9H_{17}	TXIPCH		C_9H_{17}	T5XC6H10-1E5IP	
C_9H_{17}	T4XC6H10-1E4IP		C_9H_{17}	T3XcC5H8CH2IP	
C_9H_{17}	T3XC6H10-1E3IP		C_9H_{17}	T1XIPCH	
C_9H_{17}	P8XC8H14-2E2M		C_9H_{17}	S7XC8H14-3E2M	
C_9H_{17}	S7XC8H14-2E2M		C_9H_{17}	S7XC8H14-1E7M	
C_9H_{17}	S6XC8H14-3E2M		C_9H_{17}	S6XC8H14-2E2M	
C_9H_{17}	S6XC8H14-1E7M		C_9H_{17}	S5XC8H14-3E2M	
C_9H_{17}	S5XC8H14-2E2M		C_9H_{17}	S5XC8H14-1E7M	
C_9H_{17}	S5XC6H10-1E4IP		C_9H_{17}	S5XC6H10-1E3IP	
C_9H_{17}	S5XC6H10-1E2IP		C_9H_{17}	S4XIPCH	
C_9H_{17}	S4XcC5H71M5IP		C_9H_{17}	S4XC8H14-2E2M	
C_9H_{17}	S4XC8H14-1E7M		C_9H_{17}	S4XC6H10-1E5IP	
C_9H_{17}	S4XC6H10-1E3IP		C_9H_{17}	S4XC6H10-1E2IP	
C_9H_{17}	S3XIPCH		C_9H_{17}	S3XcC5H71M5IP	
C_9H_{17}	S3XcC5H71M4IP		C_9H_{17}	S3XcC5H71M1IP	
C_9H_{17}	S3XC8H14-1E7M		C_9H_{17}	S3XC6H10-1E5IP	
C_9H_{17}	S3XC6H10-1E4IP		C_9H_{17}	S3XC6H10-1E2IP	
C_9H_{17}	S2XIPCH		C_9H_{15}	S2XcC5H51M1IP	
C_9H_{15}	S2XcC5H6-3ECH2IP		C_9H_{17}	S1XIPcC5H9	
C_9H_{17}	PXIPCH		C_9H_{17}	P8XC8H14-3E2M	
C_9H_{17}	P8XC8H14-1E7M		C_9H_{17}	P6XC6H10-1E5IP	

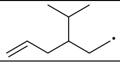
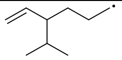
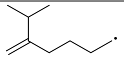
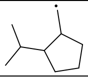
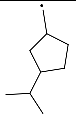
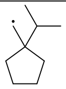
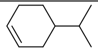
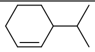
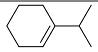
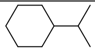
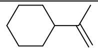
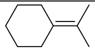
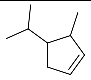
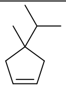
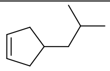
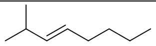
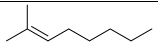
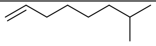
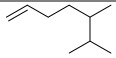
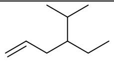
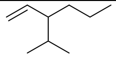
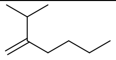
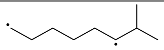
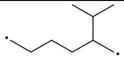
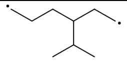
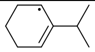
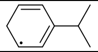
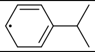
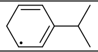
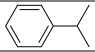
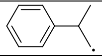
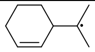
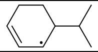
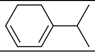
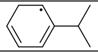
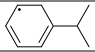
C_9H_{17}	P6XC6H10-1E4IP		C_9H_{17}	P6XC6H10-1E3IP	
C_9H_{17}	P6XC6H10-1E2IP		C_9H_{17}	P1XCH2cC5H85IP	
C_9H_{17}	P1XCH2cC5H84IP		C_9H_{17}	P1XCH2cC5H81IP	
C_9H_{16}	IPCH-3E		C_9H_{16}	IPCH-2E	
C_9H_{16}	IPCH-1E		C_9H_{18}	IPCH	
C_9H_{16}	CH2-IPCH		C_9H_{16}	CH2-2-IPCH	
C_9H_{16}	cC5H61M5IP		C_9H_{16}	cC5H61M1IP	
C_9H_{16}	cC5H7-3ECH2IP		C_9H_{18}	C8H15-3E2M	
C_9H_{18}	C8H15-2E2M		C_9H_{18}	C8H15-1E7M	
C_9H_{18}	C6H11-1E5IP		C_9H_{18}	C6H11-1E4IP	
C_9H_{18}	C6H11-1E3IP		C_9H_{18}	C6H11-1E2IP	
C_9H_{18}	int1		C_9H_{18}	int2	
C_9H_{18}	int3		C_9H_{15}	S6XIPCH-1E	
C_9H_{14}	IPCH-15E		C_9H_{13}	S4XIPCH-15E	
C_9H_{13}	S3XIPCH-15E		C_9H_{12}	A1IP	
C_9H_{11}	PXA1IP		C_9H_{15}	T1XIPCH-2E	
C_9H_{15}	S2XIPCH-3E		C_9H_{14}	IPCH-13E	
C_9H_{13}	S6XIPCH-13E		C_9H_{13}	S5XIPCH-13E	

Figure 3.44: Nomenclature and structure of the species in the mechanism.

3.5.2 Mechanism

!***

! base model, ethylcyclohexane pyrolysis and oxidation model, Wang et al., Combustion and Flame 162 (2015) 2873–2892

! add IPCH submechanism

!Reaction mechanism

ELEMENTS

H C AR

END

SPECIES

!=====C0

AR H H2

!=====C1

C CH CH2 CH2* CH3 CH4

!=====C2

C2H C2H2 H2CC C2H3 C2H4 C2H5 C2H6

!=====C3

C3H2 C3H3 aC3H4 pC3H4 aC3H5 CH3CCH2 CH3CHCH C3H6 nC3H7 iC3H7 C3H8

!=====C4

C4H C4H2 nC4H3 iC4H3 C4H4 nC4H5 iC4H5 C4H5-2 c-C4H5 C4H6 C4H612 C4H6-2 SAXC4H7 C4H7 iC4H7 iC4H7-1 C4H7-2 CH3CCHCH3 C4H8-1 C4H8-2 iC4H8 pC4H9 sC4H9 tC4H9 iC4H9

!=====C5

P1XCH2C4H5-13E S4XC4H4-13E2M S1XC4H4-13E2M T4XC5H7-13E T1XC5H7-13E C5H8-14E C5H8-13E C5H8-12E C4H5-13E2M S3XC5H9-1E P5XC5H9-1E S4XC5H9-1E S4XC5H9-2E P5XC5H9-2E P4XC4H6-1E2M P4XC4H6-1E3M C5H10-1E C5H10-2E P1XC5H11 S2XC5H11 S3XC5H11 cC5H7 PAXCH2-2-1C4H7 P1XC4H82M

C4H7-1E3M C4H7-2E2M P4XC4H6-2E2M P4XC4H83M S2XC4H83M T2XC4H6-1E3M S1XC4H6-1E3M

!=====C6

S1XcC6H7-24E C6H8-135E cC6H8-13E S2XcC6H9-1E S3XC6H9-15E P6XC6H9-13E S5XC6H9-13E cC6H10 C6H10-13E C6H10-15E cC6H11 P1XCH2cC5H9 S3XcC5H81M P6XC6H11-1E S5XC6H11-1E S4XC6H11-1E S3XC6H11-1E P5XC5H8-1E4M C6H12-1E cC6H12 S3XcC6H9-1E cC6H8-14E

C2H3-2-PXC4H6 C2H3-3-PXC4H6 C6H10-14E P6XC6H11-2E P6XC6H11-3E PXC2H4-2-1C4H7 PXCH2-3-1C5H9 S4XC6H11-2E CH3S2XcC5H8 P5XC5H8-1E3M CH2-3-C6H8-14 S3XC5H102M S3XC5H8-1E4M P5XC5H8-2E2M P3XC3H4-1E2IP P1XCH2C4H6-1E3M P1XC5H104M P1XC5H8-2E4M P1XC4H723M C6H12-2E C5H9-2E2M C5H7-13E4M C5H9-1E4M C5H9-2E4M cC5H74M cC5H75M S3XcC5H64M S3XcC5H65M C4H6-1E23M

!=====C7

CH2cC6H6-13E CH2cC6H6-25E S5XMCH-13E S4XMCH-15E S3XMCH-15E S6XMCH-13E T1XMCH-35E S2XMCH-35E CH2S2XcC6H7-5E CH2S4XcC6H7-5E MCH-13E MCH-15E MCH-35E CH2cC6H8-2E C6H7-135E3M C6H7-135E2M C7H10-135E S3XMCH-1E S2XMCH-6E T1XMCH-2E S2XMCH-3E S5XMCH-3E S2XMCH-3E CH2S2XcC6H9 S3XC7H11-16E S3XC7H11-15E S4XC7H11-15E S7XC7H11-15E T3XC6H8-15E3M S3XC6H8-15E2M S4XC6H8-15E3M P1XCH2-3C6H9-15E S4XC6H8-15E2M P1XCH2C6H9-15E C7H12-13E C7H12-16E C7H12-15E C7H12-24E C6H9-15E3M CH2-3-C6H10-1E C6H9-15E2M C6H9-13E5M CH2cC6H10 MCH-1E MCH-2E MCH-3E PXCH2cC6H11 T1XMCH S2XMCH S3XMCH S4XMCH P6XC6H10-1E2M P7XC7H13-2E P6XC6H10-1E3M S6XC7H13-1E P7XC7H13-1E S3XC7H13-1E P6XC6H10-1E4M P6XC6H10-1E5M S3XC6H10-1E5M S4XC7H13-2E S3XC6H10-1E4M S3XC6H10-1E2M T3XC6H10-1E3M MCH C7H14-1E C7H14-2E C6H11-1E2M C6H11-1E3M C6H11-1E4M C6H11-1E5M

C2H3TXcC5H8 C2H3S2XcC5H8 C2H3S3XcC5H8 P7XC7H11-13E S3XC7H11-16E CH2S3XcC6H9 CH2S4XcC6H9 CH2-4-PXC6H9 CH2-5-PXC6H9 C2H3-2-PXC5H8 C2H3cC5H9 PAXCH2-2-1C6H11

C4H5-13E2IP C4H7-1E2IP C5H8-1E34M C6H9-14E5M C6H11-3E2M P4XC4H6-1E2IP P4XC4H6-1E3IP P6XC6H10-2E2M S4XC6H10-1E5M P1XC6H10-3E5M

! ECH Species

!=====C8

!C8H9

CH2CH-1-SAXcC6H6 CH2CH-2-SAXcC6H6 CH2CH-3-SAXcC6H6 CH2CH-4-SAXcC6H6 CH2CH-5-SAXcC6H6 !C8H10

CH2CH-1-cC6H7-13 CH2CH-2-cC6H7-13 !C8H11

CH2CH-2-SAXcC6H8 CH2CH-1-SAXcC6H8 C2H5-1-SAXcC6H6 C2H5-4-SAXcC6H6 CH3CH-1-cC6H7-13 C2H5-3-SAXcC6H6 C2H5-2-SAXcC6H6 CH3CH-2-cC6H7-13 C2H5-6-SAXcC6H6 C2H5-5-SAXcC6H6 !C8H12

C2H5-1-cC6H7-13 C2H5-2-cC6H7-13 C2H5-5-cC6H7-13 !C8H13

CH2CH-1-cC6H10 C2H5-1-SAXcC6H8 C2H5-2-SAXcC6H8 CH3CH-1-cC6H9 C2H5-4-SAXcC6H8 C2H5-3-SAXcC6H8 C2H5-5-SAXcC6H8 C2H5-6-SAXcC6H8 C2H3-2-PXC6H10 CH2CH-2-cC6H10 CH2CH-3-cC6H10 CH2CH-4-cC6H10 PXC8H13-13 C2H3-3-PXC6H10 SAXC8H13-17 C2H3-4-PXC6H10 C2H3-5-PXC6H10 !C8H14

CH2CHcC6H11 CH3CHcC6H10 C2H5-1-cC6H9 C2H5-3-cC6H9 C2H5-4-cC6H9 C8H14-13E C2H3-2-1C6H11 CH3CH-2-1C6H11

!C8H15

P8XC8H15-2E C2H5-2-PXC6H10 C2H5-3-PXC6H10 P8XC8H15-3E PXC2H4-4-1C6H11 S6XC8H15-1E PXCH2-5-1C7H13 S4XC8H15-2E C2H5-2-SAX1C6H10 C2H5-3-TAX1C6H10 S5XC8H15-3E C2H5-4-SAX1C6H10 S3XC7H12-1E5M P8XC8H15-

1E S3XC8H15-1E SXC2H4cC6H11 PXC2H4cC6H11 C2H5TXcC6H10 C2H5S2XcC6H10 C2H5S3XcC6H10 C2H5S4XcC6H10 C3H7-3-SXC5H8 C2H5-3-SXC6H10 C2H5-4-SXC6H10 P7XC7H12-1E3M T3XC7H12-1E3M P8XC8H15-4E C2H5-3-S2XC6H10

!C8H16

C8H16-1E C8H16-2E C8H16-3E C7H13-1E5M C2H5cC6H11

S1XcC5H65IP C8H14-16E C7H11-15E6M C7H11-15E5M C7H11-14E6M C5H7-14E3IP C5H7-14E2IP C5H7-13E3C3H7 C8H14-17E

! aromatic species

!=====C5

C5H3 cC5H4 C5H4 lC5H5 C5H5 C5H6 lC5H7 C5H52 C5H2

!=====C6

A1 A1- l-C6H4 o-C6H4 n-C6H5 fulvene C6H2 C6H3

!=====C7

A1CH3 A1CH2 C7H6 C7H5 C5H5CH2-2 C5H5CH2-3 C5H5CH2-1 C6H4CH3 A1CH

cC5H5-13E1M cC5H5-13E5M

!=====C8

A1CC A1C2H- C6H3C2H A1C2H A1cC2H2 A1CCH2 A1CHCH C6H4C2H3 A1C2H5 A1CH2CH2 A1CHCH3 A1C2H3 C6H4C2H5

!=====C9

C9H7 C9H8 C9H9-1 C9H10

TXIPCH T5XC6H10-1E5IP T4XC6H10-1E4IP T3XcC5H8CH2IP T3XC6H10-1E3IP T1XIPCH P8XC8H14-2E2M S7XC8H14-3E2M S7XC8H14-2E2M S7XC8H14-1E7M S6XC8H14-3E2M S6XC8H14-2E2M S6XC8H14-1E7M S5XC8H14-3E2M S5XC8H14-2E2M S5XC8H14-1E7M S5XC6H10-1E4IP S5XC6H10-1E3IP S5XC6H10-1E2IP S4XIPCH S4XcC5H71M5IP S4XC8H14-2E2M S4XC8H14-1E7M S4XC6H10-1E5IP S4XC6H10-1E3IP S4XC6H10-1E2IP S3XIPCH S3XcC5H71M5IP S3XcC5H71M4IP S3XcC5H71M1IP S3XC8H14-1E7M S3XC6H10-1E5IP S3XC6H10-1E4IP S3XC6H10-1E2IP S2XIPCH S2XcC5H51M1IP S2XcC5H6-3ECH2IP S1XIPcC5H9 PXIPCH P8XC8H14-3E2M P8XC8H14-1E7M P6XC6H10-1E5IP P6XC6H10-1E4IP P6XC6H10-1E3IP P6XC6H10-1E2IP P1XCH2cC5H85IP P1XCH2cC5H84IP P1XCH2cC5H81IP IPCH-3E IPCH-2E IPCH-1E IPCH CH2-IPCH CH2-2-IPCH cC5H61M5IP cC5H61M1IP cC5H7-3ECH2IP C8H15-3E2M C8H15-2E2M C8H15-1E7M C6H11-1E5IP C6H11-1E4IP C6H11-1E3IP C6H11-1E2IP int1 int2 int3

!=====aromatic

S6XIPCH-1E IPCH-15E S4XIPCH-15E S3XIPCH-15E A1IP PXA1IP T1XIPCH-2E S2XIPCH-3E IPCH-13E S6XIPCH-13E S5XIPCH-13E

REACTIONS

! CH reactions

CH+H = C+H2 1.100E+14 0.000 0.00 ! GRI

```
CH+H2 = CH2+H 1.107E+08 1.790 1670.00 ! GRI
! CH2(triplet) reactions
CH2+H(+M) = CH3(+M) 2.500E+16 -0.800 0.00 ! GRI
LOW / 3.200E+27 -3.140 1230.00/
TROE/ 0.6800 78.00 1995.0 5590.0 /
H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/
CH2+H2 = H+CH3 5.000E+05 2.000 7230.00 ! GRI
CH2+C = C2H+H 5.000E+13 0.000 0.00 ! GRI
CH2+CH = C2H2+H 4.000E+13 0.000 0.00 ! GRI
CH2+CH2 = C2H2+H2 3.200E+13 0.000 0.00 ! GRI
! CH2(singlet) reactions
CH2*+AR = CH2+AR 9.000E+12 0.000 600.00 ! GRI
CH2*+H = CH+H2 3.000E+13 0.000 0.00 ! GRI
CH2*+H2 = CH3+H 7.000E+13 0.000 0.00 ! GRI
! CH3 reactions
CH3+H(+M) = CH4(+M) 1.270E+16 -0.630 383.00 ! GRI
LOW / 2.477E+33 -4.760 2440.00 /
TROE/ 0.7830 74.00 2941.00 6964.0 /
H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/
CH3+C = C2H2+H 5.000E+13 0.000 0.00 ! GRI
CH3+CH = C2H3+H 3.000E+13 0.000 0.00 ! GRI
CH3+CH2 = C2H4+H 4.000E+13 0.000 0.00 ! GRI
CH3+CH2* = C2H4+H 1.200E+13 0.000 -570.00 ! GRI
CH3+CH3(+M) = C2H6(+M) 2.120E+16 -0.970 620.00 ! GRI
LOW / 1.770E+50 -9.670 6220.00/
TROE/ 0.5325 151.0 1038.00 4970.0 /
H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/
CH3+CH3 = H+C2H5 4.990E+12 0.100 10600.00 ! GRI
CH3+C2H = C3H3+H 2.41E+13 0.0 0.0 ! 1986 TSA/HAM
! CH4 reactions
CH4+H = CH3+H2 6.600E+08 1.620 10840.00 ! GRI
CH4+CH = C2H4+H 6.000E+13 0.000 0.00 ! GRI
CH4+CH2 = CH3+CH3 2.460E+06 2.000 8270.00 ! GRI
CH4+CH2* = CH3+CH3 1.600E+13 0.000 -570.00 ! GRI
CH4+C2H = C2H2+CH3 1.810E+12 0.0 500.0 ! 1986 TSA/HAM
! C2H reactions
C2H+H(+M) = C2H2(+M) 1.000E+17 -1.000 0.00 ! GRI
LOW / 3.750E+33 -4.800 1900.00/
TROE/ 0.6464 132.00 1315.00 5566.0/
H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/
```

C2H+H2 = H+C2H2 4.900E+05 2.500 560.00 ! GRI

! C2H2 reactions

C2H2 (+M) = H2CC (+M) 8.000E+14 -0.520 50750.00 ! 1999 Laskin&Wang LOW / 2.450E+15 -0.640 49700.0/

H2/2.0/ CH4/2.0/ C2H6/3.0/C2H2/2.5/ C2H4/2.5/

C2H3 (+M) = C2H2+H (+M) 3.860E+08 1.620 37048.2 ! 1996 Knyazev&Slagle

LOW / 2.565E+27 -3.400 35798.72/

TROE/ 1.9816 5383.7 4.2932 -0.0795 /

H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/C2H2/3.00/ C2H4/3.00/

! Vinylidene reactions

H2CC+H = C2H2+H 1.000E+14 0.000 0.00 ! USC Mech V2.0 Estimated

! C2H3 reactions

C2H3+H(+M) = C2H4(+M) 6.080E+12 0.270 280.00 ! GRI1.2

LOW / 1.400E+30 -3.860 3320.00/

TROE/ 0.7820 207.50 2663.00 6095.00/

H2/2.0/ CH4/2.0/ C2H6/3.0/AR/0.7/ C2H2/3.00/ C2H4/3.00/

C2H3+H = C2H2+H2 9.000E+13 0.000 0.00 ! 1986 TSA/HAM

C2H3+H = H2CC+H2 6.000E+13 0.000 0.00 ! USC Mech V2.0 Estimated

C2H3+CH3 = C2H2+CH4 3.920E+11 0.000 0.00 ! 1986 TSA/HAM

C2H3+C2H3 = C2H2+C2H4 9.600E+11 0.00 0. ! NIST Database

! C2H4 reactions

C2H4+H(+M) = C2H5(+M) 1.367E+09 1.463 1355.00 !04-MIL-KLI

LOW / 2.027E+39 -6.642 5769.00 /

TROE / -0.569 299.0 9147.0 -152.40 /

H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/

C2H4(+M)=H2+C2H2(+M) 8.00E+12 0.44 88770. ! GRI3.0

LOW / 1.58E+51 -9.30 97800./

TROE / 0.7345 180 1035 5417/

H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/

C2H4+H = C2H3+H2 5.070E+07 1.900 12950.00 ! 1996 Knyazev et al.

C2H4+CH = aC3H4+H 3.000E+13 0.000 0.00 ! USC Mech V2.0 Estimated

C2H4+CH = pC3H4+H 3.000E+13 0.000 0.00 ! USC Mech V2.0 Estimated

C2H4+CH2 = aC3H5+H 2.000E+13 0.000 6000.00 ! USC Mech V2.0 Estimated

C2H4+CH2* = H2CC+CH4 5.000E+13 0.000 0.00 ! USC Mech V2.0 Estimated

C2H4+CH2* = aC3H5+H 5.000E+13 0.000 0.00 ! USC Mech V2.0 Estimated

C2H4+CH3 = C2H3+CH4 2.270E+05 2.000 9200.00 ! GRI

C2H4+C2H = C4H4+H 1.200E+13 0.000 0.00 ! 1986 TSA/HAM

! C2H5 reactions

```
C2H5+H(+M) = C2H6(+M) 5.210E+17 -0.990 1580.00 ! GRI
LOW / 1.990E+41 -7.080 6685.00/
TROE / 0.8422 125.0 2219.00 6882.0/
H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/
C2H5+H = C2H4+H2 2.000E+12 0.000 0.00 ! GRI
C2H5+CH3(+M) = C3H8(+M) 4.90E+14 -0.50 0.0 ! 1988 TSA
LOW / 6.80E+61 -13.42 6000.0/
TROE / 1.000 1000.0 1433.9 5328.8 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
! C2H6 reactions
C2H6+H = C2H5+H2 1.15E+08 1.900 7530.00 ! GRI
C2H6+CH2* = C2H5+CH3 4.00E+13 0.000 -550.00 ! GRI
C2H6+CH3 = C2H5+CH4 6.14E+06 1.740 10450.00 ! GRI
C2H6+C2H=C2H2+C2H5 3.61E+12 0.00 0 ! 1986 TSA/HAM
C2H6+C2H3=C2H4+C2H5 6.01E+02 3.30 10502 ! 1986 TSA/HAM
! C3H2 reactions
C3H2+H(+M)=C3H3(+M) 1.02e+13 0.27 279.64 ! 2009 Blanquart et al.
LOW/ 2.80e+30 -3.860 3319.79/
TROE/ 0.782 207.50 2663.00 6095.00/
H2/2.00/ AR/0.70/CH4/2.00/ C2H6/3.00/
C3H2+CH=C4H2+H 5.00E+13 0.0 0. ! USC Mech V2.0
!C3H3 reactions
C3H3+H = C3H2+H2 1.00E+13 0.0 1000. ! USC Mech V2.0
C2H2+CH2 = C3H3+H 1.20E+13 0.00 6620.00 ! 1988 Bohland et al.; 1988 Frank et al.
C2H2+CH2* = C3H3+H 2.00E+13 0.00 0.00 ! 1997 Wang&Frenklach
! C3H4 reactions
! aC3H4=pC3H4 6.0256E+53 -12.18 84276. ! J. A. Miller Mechanism
! PLOG /0.03947 6.0256E+53 -12.18 84276./
! PLOG /1. 7.7625E+39 -7.80 78446./
! PLOG /10. 4.7863E+48 -10.0 88685./
C3H3+H=pC3H4 3.6308E+36 -7.36 6039. ! J. A. Miller Mechanism
PLOG /0.03947 3.6308E+36 -7.36 6039./
PLOG /1. 7.943E+29 -5.06 4861./
PLOG /10. 1.072E24 -3.15 3261./
C3H3+H=aC3H4 3.3884E+36 -7.41 6337. ! J. A. Miller Mechanism
PLOG /0.03947 3.3884E+36 -7.41 6337./
PLOG /1. 3.1623E+29 -5. 4711./
PLOG /10. 8.7096E+23 -3.20 3255./
aC3H4+H = C3H3+H2 6.60E+03 3.1 5522 ! 2008 Miller 30 Torr
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aC3H4+CH3=C3H3+CH4 6.600E-4 5.000 8300 ! 2009 Kiefer et al.

H+aC3H4 = H+pC3H4 1.47E+13 0.26 4103 ! 2008 Miller 30 Torr

aC3H4+C2H = C2H2+C3H3 1.00E+13 0.0 0.0 ! 1997 Wang&Frenklach

! H+aC3H4 = CH3+C2H2 2.72E+09 1.2 6834 ! 2008 Miller 30 Torr

pC3H4+H = C3H3+H2 3.57E+04 2.8 4821 ! 2008 Miller 30 Torr !

pC3H4+CH3=C3H3+CH4 2.200E-4 5.000 8300 ! 2009 Kiefer et al.

pC3H4+C3H3 = aC3H4+C3H3 6.14E+06 1.74 10450. ! USC Mech V2.0 Estimated

pC3H4+C2H = C2H2+C3H3 1.00E+13 0.0 0.0 ! USC Mech V2.0 Estimated

! H+pC3H4 = C2H2+CH3 3.89E+10 0.989 4114 ! 2008 Miller 30 Torr

C2H2+CH3 = pC3H4+H 2.51E+11 0.56 11453.0 !99DAV/LAW RRKM !99DAV/LAW RRKM ! activatin energy decrease 4 kcal/mol in this work

! PLOG / 0.1 4.50E+06 1.86 11600.0 / !99DAV/LAW RRKM 0.1 atm

! PLOG / 1 2.56E+09 1.10 13644.0 / !99DAV/LAW RRKM 1 atm

! PLOG / 2 2.07E+10 0.85 14415.0 / !99DAV/LAW RRKM 2 atm

! PLOG /5 2.51E+11 0.56 15453.0 / !99DAV/LAW RRKM 5 atm

! PLOG /10 1.10E+12 0.39 16200.0 / !99DAV/LAW RRKM 10 atm

! PLOG /100 2.10E+12 0.37 18100.0 / !99DAV/LAW RRKM 100 atm

C2H2+CH3 = aC3H4+H 2.40E+09 0.91 20700.0 !

! PLOG /0.1 2.40E+09 0.91 20700.0 / !99DAV/LAW RRKM 0.1 atm

! PLOG /1 5.14E+09 0.86 22153.0 / !99DAV/LAW RRKM 1 atm

! PLOG /2 1.33E+10 0.75 22811.0 / !99DAV/LAW RRKM 2 atm

! PLOG /5 9.20E+10 0.54 23950.0 / !99DAV/LAW RRKM 5 atm

! PLOG /10 5.10E+11 0.35 25000.0 / !99DAV/LAW RRKM 10 atm

! PLOG /100 7.30E+12 0.11 28500.0 / !99DAV/LAW RRKM 100 atm

pC3H4 = aC3H4 6.40E+61 -14.59 88200.0 !99DAV/LAW RRKM

PLOG /0.1 6.40E+61 -14.59 88200.0 / !99DAV/LAW RRKM 0.1 atm

PLOG/ 0.4 5.81E+62 -14.63 91211.0 / !99DAV/LAW RRKM 0.4 atm

PLOG/ 1.0 5.15E+60 -13.93 91117.0 / !99DAV/LAW RRKM 1 atm

PLOG/ 2.0 7.64E+59 -13.59 91817.0 / !99DAV/LAW RRKM 2 atm

PLOG/ 5.0 3.12E+58 -13.07 92680.0 / !99DAV/LAW RRKM 5 atm

PLOG/ 10.0 1.90E+57 -12.62 93300.0 / !99DAV/LAW RRKM 10 atm

PLOG/ 100 1.40E+52 -10.86 95400.0 / !99DAV/LAW RRKM 100 atm

! CH3CHCH CH3CCH2 and aC3H5 reactions

CH3CHCH+H = aC3H5+H 1.47E+13 0.26 4103 ! Ref H+aC3H4=H+pC3H4

CH3CCH2+H = pC3H4+H2 3.34E+12 0.00 0.0 ! 1999 Davis et al.

CH3CCH2+H = aC3H5+H 1.47E+13 0.26 4103 ! Ref aC3H4+H=pC3H4+H

CH3CCH2+CH3 = pC3H4+CH4 1.00E+11 0.00 0.0 ! 1999 Davis et al.

aC3H5+H = aC3H4+H2 9.56E+03 2.80 3291.11 ! 2009 Blanquart et al.

aC3H5+CH3 = aC3H4+CH4 1.50E+12 -0.32 -131.0 ! 1991 TSA 3.00E+12/2

C2H5+C2H3 = aC3H5+CH3 8.00E+25 -3.46 11775.0 ! 1986 TSA/HAM RRKM 0.1 atm
aC3H4+H = CH3CHCH 1.10E+30 -6.52 15200.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 5.05E+29 -6.52 15200.0 / ! EST 0.1 atm /2
PLOG / 0.1 1.10E+30 -6.52 15200.0 /
PLOG / 1.0 5.40E+29 -6.09 16300.0 /
PLOG / 10.0 2.60E+31 -6.23 18700.0 /
PLOG / 100.0 3.20E+31 -5.88 21500.0 /
pC3H4+H = CH3CHCH 1.00E+25 -5.00 1800.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 5.0E+24 -5.00 1800.0 / ! EST 0.1 atm /2
PLOG / 0.1 1.00E+25 -5.00 1800.0 /
PLOG / 1.0 5.50E+28 -5.74 4300.0 /
PLOG / 10.0 1.00E+34 -6.88 8900.0 /
PLOG / 100.0 9.70E+37 -7.63 13800.0 /
C2H2+CH3 = CH3CHCH 1.40E+32 -7.14 10000.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 7.0E+31 -7.14 10000.0 / ! EST 0.1 atm /2
PLOG / 0.1 1.40E+32 -7.14 10000.0 /
PLOG / 1.0 3.20E+35 -7.76 13300.0 /
PLOG / 10.0 2.40E+38 -8.21 17100.0 /
PLOG / 100.0 1.40E+39 -8.06 20200.0 /
aC3H4+H = CH3CCH2 9.20E+38 -8.65 7000.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 4.60E+38 -8.65 7000.0 / ! EST 0.1 atm /2
PLOG / 0.1 9.20E+38 -8.65 7000.0 /
PLOG / 1.0 9.46E+42 -9.43 11190.0 /
PLOG / 2.0 8.47E+43 -9.59 12462.0 /
PLOG / 5.0 6.98E+44 -9.70 14032.0 /
PLOG / 10.0 1.50E+45 -9.69 15100.0 /
PLOG / 100.0 1.80E+43 -8.78 16800.0 /
pC3H4+H = CH3CCH2 4.60E+44 -10.21 10200.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 2.30E+44 -10.21 10200.0 / ! EST 0.1 atm /2
PLOG / 0.1 4.60E+44 -10.21 10200.0 /
PLOG / 1.0 1.66E+47 -10.58 13690.0 /
PLOG / 2.0 5.04E+47 -10.61 14707.0 /
PLOG / 5.0 9.62E+47 -10.55 15910.0 /
PLOG / 10.0 7.00E+47 -10.40 16600.0 /
PLOG / 100.0 3.20E+44 -9.11 17400.0 /
C2H2+CH3 = CH3CCH2 6.80E+20 -4.16 18000.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 3.40E+20 -4.16 18000.0 / ! EST 0.1 atm /2
PLOG / 0.1 6.80E+20 -4.16 18000.0 /
PLOG / 1.0 4.99E+22 -4.39 18850.0 /

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PLOG / 2.0 6.00E+23 -4.60 19571.0 /
PLOG / 5.0 7.31E+25 -5.06 21150.0 /
PLOG / 10.0 9.30E+27 -5.55 22900.0 /
PLOG / 100.0 3.80E+36 -7.58 31300.0 /
CH3CCH2 = CH3CHCH 1.60E+44 -12.16 52200.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 8.0E+43 -12.16 52200.0 / ! EST 0.1 atm /2
PLOG / 0.1 1.60E+44 -12.16 52200.0 /
PLOG / 1.0 1.50E+48 -12.71 53900.0 /
PLOG / 10.0 5.10E+52 -13.37 57200.0 /
PLOG / 100.0 5.80E+51 -12.43 59200.0 /
aC3H5 = CH3CHCH 1.30E+55 -14.53 73800.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 6.50E+54 -14.53 73800.0 / ! EST 0.1 atm /2
PLOG / 0.1 1.30E+55 -14.53 73800.0 /
PLOG / 1.0 5.00E+51 -13.02 73300.0 /
PLOG / 10.0 9.70E+48 -11.73 73700.0 /
PLOG / 100.0 4.86E+44 -9.84 73400.0 /
aC3H5 = CH3CCH2 3.90E+59 -15.42 75400.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 1.45E+59 -15.42 75400.0 / ! EST 0.1 atm /2
PLOG / 0.1 3.90E+59 -15.42 75400.0 /
PLOG / 1.0 7.06E+56 -14.08 75868.0 /
PLOG / 2.0 4.80E+55 -13.59 75949.0 /
PLOG / 5.0 4.86E+53 -12.81 75883.0 /
PLOG / 10.0 6.40E+51 -12.12 75700.0 /
PLOG / 100.0 2.80E+43 -9.27 74000.0 /
C2H2+CH3=aC3H5 8.2E+53 -13.32 33200. ! 1999 Davis et al. RRKM
PLOG /0.039 4.1E+53 -13.32 33200. / ! EST 0.1 atm /2
PLOG /0.1 8.2E+53 -13.32 33200. /
PLOG /1.0 2.7E+53 -12.82 35700. /
PLOG /10.0 4.4E+49 -11.40 36700. /
PLOG /100.0 3.8E+44 -9.63 37600. /
pC3H4+H=aC3H5 1.1E+60 -14.56 28100. ! 1999 Davis et al. RRKM
PLOG /0.039 5.5E+59 -14.56 28100. / ! EST 0.1 atm /2
PLOG /0.1 1.1E+60 -14.56 28100. /
PLOG /1.0 4.9E+60 -14.37 31600. /
PLOG /10.0 2.2E+59 -13.61 34900. /
PLOG /100.0 1.6E+55 -12.07 37500. /
!aC3H4+H=aC3H5 9.60E+61 -14.67 26000.0 ! 1999 Davis et al. RRKM
!PLOG / 0.039 4.80E+61 -14.67 26000.0 / ! EST 0.1 atm /2
!PLOG / 0.1 9.60E+61 -14.67 26000.0 /
!PLOG / 1.0 1.52E+59 -13.54 26949.0 /
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!PLOG / 2.0 3.78E+57 -12.98 26785.0 /
!PLOG / 5.0 7.34E+54 -12.09 26187.0 /
!PLOG / 10.0 2.40E+52 -11.30 25400.0 /
!PLOG / 100.0 6.90E+41 -8.06 21300.0 /
aC3H5=aC3H4+H 1.76E+58 -13.715 76013
PLOG / 0.039 8.80E+57 -13.715 76013/ ! 2009 Kiefer et al./2
PLOG / 0.066 2.53E+58 -13.661 76765/ ! 2009 Kiefer et al.
PLOG / 0.132 4.34E+58 -13.628 77634/ ! 2009 Kiefer et al.
PLOG / 0.197 8.07E+58 -13.645 78292/ ! 2009 Kiefer et al.
PLOG / 0.263 1.49E+59 -13.677 78833/ ! 2009 Kiefer et al.
PLOG / 1 1.30E+67 -15.61 88301/ ! 2005 Fernandes et al.
PLOG / 4 6.80E+64 -14.75 89043/ ! 2005 Fernandes et al.
PLOG / 100 1.5E+15 0 63541/ ! 2005 Fernandes et al.
aC3H5+aC3H5 = pC3H4+C3H6 8.43E+10 0.0 -263 !2009 Kifer et al
!C3H6 reactions
aC3H5+H(+M) = C3H6(+M) 2.00E+14 0.00 0.0 ! 1991 TSA
LOW / 1.33E+60 -12.00 5967.8 /
TROE / 0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C2H3+CH3 (+M) = C3H6(+M) 2.50E+13 0.000 0.00 ! 1986 TSA/HAM
LOW / 4.270E+58 -11.940 9769.80 /
TROE / 0.175 1340.6 60000.0 10139.8 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/C2H2/3.00/ C2H4/3.00/
C3H6 = H2 + pC3H4 1.18E+95 -23.6 125649 ! 2009 Kiefer et al.
C3H6 = H2 + aC3H4 1.18E+95 -23.6 125649 ! ref:C3H6 = H2 + pC3H4
C3H6+H = C2H4+CH3 8.80E+16 -1.05 6461.0 ! 1991 TSA
C3H6+H = aC3H5+H2 1.73E+05 2.50 2490.0 ! 1991 TSA
C3H6+H = CH3CCH2+H2 4.00E+05 2.50 9790.0 ! 1991 TSA
C3H6+H = CH3CHCH+H2 8.04E+05 2.50 12283.0 ! 1991 TSA
C3H6+CH3 = aC3H5+CH4 2.20E+00 3.50 5675.0 ! 1991 TSA
C3H6+CH3 = CH3CCH2+CH4 8.40E-01 3.50 11660.0 ! 1991 TSA
C3H6+CH3 = CH3CHCH+CH4 1.35E+00 3.50 12848.0 ! 1991 TSA
C3H6+C2H3 = C4H6+CH3 7.23E+11 0.0 5000.0 ! 1991 TSA
! reactions of nC3H7
nC3H7+H(+M) = C3H8(+M) 3.60E+13 0.00 0.0 ! 1988 TSA
LOW / 3.01E+48 -9.32 5833.6/
TROE / 0.498 1314.0 1314.0 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C3H6+H(+M) = nC3H7(+M) 1.33E+13 0.00 3260.7 ! 1991 TSA
LOW / 6.26E+38 -6.66 7000.0/
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TROE / 1.000 1000.0 1310.0 48097.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
CH3+C2H4(+M)= nC3H7(+M) 2.55E+06 1.600 5700. ! 1988 TSA
LOW / 3.00E+63 -14.6 18170./
TROE /0.1894 277. 8748. 7891./
H2/2.00/ CH4/2.00/ C2H6/3.00/ AR/0.70/
nC3H7+H = C2H5+CH3 3.40E+18 -1.33 5386.0 ! 1988 TSA
nC3H7+H = C3H6+H2 1.80E+12 0.00 0.0 ! 1988 TSA
nC3H7+CH3 = CH4+C3H6 1.10E+13 -0.32 0.0 ! 1988 TSA
! reactions of iC3H7
iC3H7+H(+M) = C3H8(+M) 2.40E+13 0.00 0.0 ! 1988 TSA
LOW / 1.70E+58 -12.08 11263.7/
TROE / 0.649 1213.1 1213.1 13369.7 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C3H6+H(+M) = iC3H7(+M) 1.33E+13 0.00 1559.8 ! 1991 TSA
LOW / 8.70E+42 -7.50 4721.8/
TROE / 1.000 1000.0 645.4 6844.3/
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
iC3H7+H = CH3+C2H5 5.90E+23 -2.81 10009.0 ! 1988 TSA RRKM 0.1 atm
iC3H7+H = C3H6+H2 3.20E+12 0.00 0.0 ! 1988 TSA
iC3H7+CH3 = CH4 + C3H6 9.4E+10 0.68 0.0 ! 1988 TSA
! reactions of C3H8
C3H8+H = H2+nC3H7 1.30E+06 2.54 6756.0 ! 1988 TSA
C3H8+H = H2+iC3H7 1.30E+06 2.40 4471.0 ! 1988 TSA
C3H8+CH3 = CH4+nC3H7 9.03E-01 3.65 7153.0 ! 1988 TSA
C3H8+CH3 = CH4+iC3H7 1.51E+00 3.46 5480.0 ! 1988 TSA
! reactions of C4H2
C2H2+C2H2 = C4H2+H2 1.50E+13 0.0 42700 ! 2007 Gueniche et al.
C2H2+C2H = C4H2+H 9.60E+13 0.00 0.00 ! 1991 SHI/MIC, 1992 Koshi et al., 1993 Fahrat et al.
! reactions of nC4H3
C2H2+C2H(+M) = nC4H3(+M) 8.30E+10 0.899 -363.00 ! 1992 Wang
LOW / 1.240E+31 -4.718 1871.00/
TROE / 1.0 100. 5613. 13387./
H2/2.0/ CH4/2.0/ C2H6/3.0/ C2H2/2.5/ C2H4/2.5/
nC4H3 + H = C4H4 1.10E+42 -9.65 7000.0 ! 1997 Wang&Frenklach
PLOG / 0.026 1.10E+42 -9.65 7000.0/
PLOG / 0.118 1.10E+42 -9.65 7000.0/
PLOG / 1.0 2.00E+47 -10.26 13070.0/
C4H2 + H = nC4H3 1.70E+49 -11.67 12804.0 ! 1997 Wang&Frenklach
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PLOG / 0.026 1.70E+49 -11.67 12804.0/
PLOG / 0.118 3.30E+50 -11.80 15010.0/
PLOG / 1.0 1.10E+42 -8.72 15300.0/
nC4H3 = iC4H3 3.70E+61 -15.81 54890.0 ! 1997 Wang&Frenklach
PLOG / 0.026 3.70E+61 -15.81 54890.0/
PLOG / 0.118 1.00E+51 -12.45 51000.0/
PLOG / 1.0 4.10E+43 -9.49 53000.0/
C3H3+CH = nC4H3+H 5.00E+13 0.0 0.0 ! USC Mech V2.0 Estimated
C3H2+CH2 = nC4H3+H 5.00E+13 0.0 0.0 ! 1992 Miller&Melius
nC4H3+H = C4H2+H2 3.00E+13 0.00 0.0 ! = 0.5*C2H3+H USC Mech V2.0
nC4H3 + H = C2H2 + H2CC 1.60E+19 -1.60 2220.0 ! 1997 Wang&Frenklach 0.026 atm RRKM
nC4H3 + H = iC4H3 + H 2.40E+11 0.79 2410.0 ! 1997 Wang&Frenklach 0.026 atm RRKM
! reactions of iC4H3
C2H2+C2H(+M) = iC4H3(+M) 8.30E+10 0.899 -363.00 ! 1992 Wang
LOW / 1.240E+31 -4.718 1871.00/
TROE / 1.0 100. 5613. 13387./
H2/2.0/ CH4/2.0/ C2H6/3.0/C2H2/2.5/ C2H4/2.5/
C4H2+H(+M)=iC4H3(+M) 4.31E+10 1.160 1751.91 ! 1992 Wang
LOW / 2.30e+45 -8.100 2507.17/
TROE / 0.0748 1.00 -4216.00/
H2/2.00/ AR/0.70/ CH4/2.00/ C2H6/3.00/
iC4H3 + H = C4H4 4.20E+44 -10.27 7890.0 ! 1997 Wang&Frenklach
PLOG / 0.026 4.20E+44 -10.27 7890.0 /
PLOG / 0.118 5.30E+46 -10.68 9270.0 /
PLOG / 1.0 3.40E+43 -9.01 12120.0/
iC4H3+H = C2H2+H2CC 2.40E+19 -1.60 2800.0 ! 1997 Wang&Frenklach 0.026 atm RRKM
iC4H3+H = C4H2+H2 6.00E+13 0.00 0.0 ! = C2H3+H USC Mech V2.0
C3H3+CH = iC4H3+H 5.00E+13 0.0 0.0 ! USC Mech V2.0 Estimated
! reactions of C4H4
H2CC+C2H2(+M) = C4H4(+M) 3.50E+05 2.055 -2400. ! 1999 Laskin&Wang
LOW / 1.40E+60 -12.599 7417./
TROE / 0.98 560. 580. 4164./
H2/2.0/ CH4/2.0/ C2H2/3.0/ C2H4/3.0/ C2H6/3.0/
C2H3+C2H = C4H4 1.00E+14 0.00 0.0 ! 1988 Duran et al.
C3H3+CH2* = C4H4+H 4.00E+13 0.0 0.0 ! 2007 Gueniche et al.
C4H4+H = nC4H3+H2 6.65E+05 2.53 12240. ! 1997 Wang&Frenklach
C4H4+H = iC4H3+H2 3.33E+05 2.53 9240. ! 1997 Wang&Frenklach
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C2H3+C2H2=C4H4+H 5.00E+14 -0.71 6700. ! 1997 Wang&Frenklach 0.026 atm RRKM

C3H3+CH2=C4H4+H 5.00E+13 0.00 0.0 ! 1992 Miller&Melius

C3H2+CH3=C4H4+H 5.00E+12 0.00 0.0 ! USC Mech V2.0

! reactions of nC4H5

C2H3 + C2H2 = nC4H5 1.10E+31 -7.14 5600. ! 1997 Wang&Frenklach

PLOG / 0.013 1.10E+31 -7.14 5600. /

PLOG / 0.026 1.10E+32 -7.33 6200. /

PLOG / 0.118 2.40E+31 -6.95 5600. /

PLOG / 1.0 9.30E+38 -8.76 12000./

PLOG / 10.0 8.10E+37 -8.09 13400./

C4H4 + H = nC4H5 1.20E+51 -12.57 12300. ! 1997 Wang&Frenklach

PLOG / 0.013 1.20E+51 -12.57 12300./

PLOG / 0.026 4.20E+50 -12.34 12500./

PLOG / 0.118 1.10E+50 -11.94 13400./

PLOG / 1.0 1.30E+51 -11.92 16500./

PLOG / 10.0 6.20E+45 -10.08 15800./

nC4H5 = iC4H5 2.40E+60 -16.08 47500. ! 1997 Wang&Frenklach

PLOG / 0.013 2.40E+60 -16.08 47500./

PLOG / 0.026 1.30E+62 -16.38 49600./

PLOG / 0.118 4.90E+66 -17.26 55400./

PLOG / 1.0 1.50E+67 -16.89 59100./

PLOG / 10.0 2.00E+60 -14.46 58600./

nC4H5+H = iC4H5+H 1.00E+36 -6.26 17486. ! 1997 Wang&Frenklach 0.026 atm RRKM

C2H3+C2H3 = nC4H5+H 1.10E+24 -3.28 12395. ! 1997 Wang&Frenklach 0.026 atm RRKM

nC4H5+H = C4H4+H2 1.50E+13 0.00 0.0 ! 1997 Wang&Frenklach

! reactions of iC4H5

C2H3 + C2H2 = iC4H5 5.00E+34 -8.42 7900. ! 1997 Wang&Frenklach

PLOG / 0.013 5.00E+34 -8.42 7900. /

PLOG / 0.026 2.10E+36 -8.78 9100. /

PLOG / 0.118 1.00E+37 -8.77 9800. /

PLOG / 1.0 1.60E+46 -10.98 18600./

PLOG / 10.0 5.10E+53 -12.64 28800./

C4H4 + H = iC4H5 6.10E+53 -13.19 14200. ! 1997 Wang&Frenklach

PLOG / 0.013 6.10E+53 -13.19 14200./

PLOG / 0.026 9.60E+52 -12.85 14300./

PLOG / 0.118 2.10E+52 -12.44 15500./

PLOG / 1.0 4.90E+51 -11.92 17700./

PLOG / 10.0 1.50E+48 -10.58 18800./

C2H3+C2H3 = iC4H5+H 1.50E+30 -4.95 12958. ! 1997 Wang&Frenklach 0.026 atm RRKM

iC4H5+H = C4H4+H2 3.0E+13 0.00 0. ! 1997 Wang&Frenklach

iC4H5+H=C3H3+CH3 1.0E14 0.00 0. ! 2009 Hansen et al C3H4 FLAME

! reactions of C4H5-2

C4H5-2 = iC4H5 1.30E+62 -16.38 49600. ! nC4H5=¿iC4H5 1997 Wang&Frenklach 0.026 atm RRKM

iC4H5+H = C4H5-2+H 1.00E+36 -6.26 17486. ! = nC4H5+H=¿iC4H5+H 0.026 atm RRKM 1997 Wang&Frenklach

! Ractions of c-C4H5

c-C4H5 + H = C4H6 1.000E+13 0.000 0.00 ! Est. HW, fast c-C4H6 -¿ C4H6 - Lifshitz USC Mech V2.0

c-C4H5 + H = C2H4 + C2H2 1.000E+13 0.000 0.00 ! Est. HW USC Mech V2.0

c-C4H5 = C4H4 + H 3.000E+12 0.000 52000.00 ! Est. HW USC Mech V2.0

c-C4H5 = C2H3 + C2H2 2.000E+12 0.000 58000.00 ! Est. HW USC Mech V2.0

! reactions of C4H6

C4H6 = C4H4+H2 8.33E+13 0.0 94700. !

PLOG / 0.039 8.33E+13 0.0 94700./ ! EST 2.5E+15 /30

PLOG / 1.0 2.50E+15 0.0 94700./ ! 1996 Hidaka et al.

C4H6 = H2CC+C2H4 1.00E+13 0.0 85000.0 ! EST

C2H3 + C2H3 = C4H6 7.00E+57 -13.82 17629. ! 1997 Wang&Frenklach

PLOG / 0.026 7.00E+57 -13.82 17629./

PLOG / 0.118 1.50E+52 -11.97 16056./

PLOG / 1.0 1.50E+42 -8.84 12483./

C4H6 = iC4H5 + H 8.20E+51 -10.92 118409. ! 1997 Wang&Frenklach

PLOG / 0.026 8.20E+51 -10.92 118409./

PLOG / 0.118 3.30E+45 -8.95 115934./

PLOG / 1.0 5.70E+36 -6.27 112353./

C4H6 = nC4H5 + H 3.50E+61 -13.87 129677. ! 1997 Wang&Frenklach

PLOG / 0.026 3.50E+61 -13.87 129677./

PLOG / 0.118 8.50E+54 -11.78 127472./

PLOG / 1.0 5.30E+44 -8.62 123608./

C4H6+H = nC4H5+H2 1.33E+06 2.53 12240. ! =C2H4+H USC Mech V2.0

C4H6+H = iC4H5+H2 6.65E+05 2.53 9240. ! USC Mech V2.0 Estimated

C4H6+H = C2H4+C2H3 1.46E+30 -4.34 21647. ! USC Mech II (1997 Wang&Frenklach 1 atm)

C4H6+H = pC3H4+CH3 2.00E+12 0.0 7000. ! USC Mech V2.0 Estimated

C4H6+H = aC3H4+CH3 2.00E+12 0.0 7000. ! USC Mech V2.0 Estimated

C4H6+CH3 = nC4H5+CH4 2.00E+14 0.0 22800. ! 1996 Hidaka et al.

C4H6+CH3 = iC4H5+CH4 1.00E+14 0.0 19800. ! 1996 Hidaka et al.

C4H6+C2H3 = nC4H5+C2H4 5.00E+13 0.0 22800. ! 1996 Hidaka et al.

C4H6+C2H3 = iC4H5+C2H4 2.50E+13 0.0 19800. ! 1996 Hidaka et al.

C4H6+C3H3 = nC4H5+aC3H4 1.00E+13 0.0 22500. ! 1996 Hidaka et al.

C4H6+C3H3 = iC4H5+aC3H4 0.50E+13 0.0 19500. ! 1996 Hidaka et al.

C4H6+aC3H5 = nC4H5+C3H6 1.00E+13 0.0 22500. ! USC Mech V2.0 Estimated

C4H6+aC3H5 = iC4H5+C3H6 0.50E+13 0.0 19500. ! USC Mech V2.0 Estimated

! reactions of 1,2-C4H6

C4H612 = C4H6 1.00E+12 0.0 65000 !

PLOG / 0.039 1.00E+12 0.0 65000/ ! EST 3.00E+13 /30

PLOG / 1.0 3.00E+13 0.0 65000/ ! 1996 Hidaka et al

C3H3+CH3 (+M) = C4H612 (+M) 1.50E+12 0.0 0.0 ! 1997 Wang&Frenklach

LOW / 2.60E+57 -11.94 9770.0/

TROE / 0.175 1340.6 60000.0 9769.8 /

H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/

C4H612+H = nC4H5+H2 1.33E+06 2.53 12240. ! = C2H4+H

C4H612 = iC4H5+H 2.10E+14 0.0 92600. !

PLOG / 0.039 2.10E+14 0.0 92600./ ! EST 4.20E+15 /20

PLOG / 1.0 4.20E+15 0.0 92600./ ! 1995 Leung et al.

C4H612+H = C4H6+H 2.00E+13 0.0 4000. ! USC Mech V2.0 Estimated

C4H612+H = iC4H5+H2 1.70E+05 2.5 2490. ! = C3H6+H USC Mech V2.0

C4H612+H = aC3H4+CH3 2.00E+13 0.0 2000. ! 1997 Wang&Frenklach

C4H612+H = pC3H4+CH3 2.00E+13 0.0 2000. ! 1997 Wang&Frenklach

C4H612+CH3 = iC4H5+CH4 7.00E+13 0.0 18500. ! 1988 Kern et al.

! reactions of C4H6-2

C4H6-2 = C4H6 1.00E+12 0.000 65000. !

PLOG / 0.039 1.00E+12 0.000 65000./ ! EST 3.00E+13 /30

PLOG / 1.0 3.00E+13 0.000 65000./ ! 1996 Hidaka et al.

C4H6-2 = C4H612 1.00E+12 0.000 67000. !

PLOG / 0.039 1.00E+12 0.000 67000./ ! EST 3.00E+13 /30

PLOG / 1.0 3.00E+13 0.000 67000./ ! 1996 Hidaka et al.

C4H6-2+H = C4H612+H 2.00E+13 0.0 4000. ! USC Mech V2.0 Estimated

C4H6-2+H = C4H5-2+H2 3.40E+05 2.5 2490. ! = C3H6+H USC Mech V2.0

C4H6-2+H = CH3+pC3H4 2.60E+5 2.500 1000. ! 1996 Hidaka et al.

C4H6-2 = H+C4H5-2 1.67E+14 0.000 87300. !

PLOG / 0.039 1.67E+14 0.000 87300./ ! EST 5.00E+15 /30

PLOG / 1.0 5.00E+15 0.000 87300./ ! 1996 Hidaka et al.

C4H6-2+CH3 = C4H5-2+CH4 1.40E+14 0.0 18500. ! USC Mech V2.0 Estimated

! reactions of saxC4H7

SAXC4H7(+M) = C4H6+H(+M) 4.70E+08 1.32 44697.6 ! JetSurF 2.0

LOW / 4.6E-37 15.37 -603.1/

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

SAXC4H7+H = C4H612+H2 1.80E+13 0.0 0.0 ! EST JetSurF 2.0

C4H612+H = SAXC4H7 1.20E+10 0.69 3000 ! 2007 Gueniche et al./10

SAXC4H7+H = C4H6+H2 1.80E+13 0.00 0.0 ! (aC3H5+H) JetSurF 2.0

SAXC4H7+CH3=C4H6+CH4 3.00E+12 -0.32 -131.0 ! aC3H5+CH3 = aC3H4+CH4 JetSurF 2.0

SAXC4H7+CH3 = C4H612+CH4 1.00E+13 0.00 0.0 ! EST JetSurF 2.0

SAXC4H7+C2H3 = C4H6+C2H4 1.00E+13 0.00 0.0 ! EST JetSurF 2.0

SAXC4H7+C2H3 = C4H612+C2H4 1.00E+13 0.00 0.0 ! EST JetSurF 2.0

! reactions of C4H7

C4H7 = C4H6+H 1.27E+24 -4.75 23777 !

PLOG / 0.033 1.27E+24 -4.75 23777 / ! 2009 Kiefer et al.

PLOG / 0.066 1.38E+26 -5.221 25729 / ! 2009 Kiefer et al.

PLOG / 0.132 1.75E+28 -5.709 27764 / ! 2009 Kiefer et al.

PLOG / 0.197 3.16E+29 -6.003 28985 / ! 2009 Kiefer et al.

PLOG / 0.263 2.69E+30 -6.222 29890 / ! 2009 Kiefer et al.

PLOG / 1.0 2.48E+53 -12.30 52000 / ! 1997 Wang&Frenklach

PLOG / 10 1.85E+48 -10.50 51770 / ! 1997 Wang&Frenklach

C2H4+C2H3 = C4H7 1.23E+35 -7.76 9930.0 ! 1997 Wang&Frenklach

PLOG / 0.039 6.15E+34 -7.76 9930.0 / ! EST 0.1 atm/2

PLOG / 0.1 1.23E+35 -7.76 9930.0 /

PLOG / 1.0 7.93E+38 -8.47 14220.0/

PLOG / 10 2.99E+36 -7.40 15480.0/

C4H7+H = SAXC4H7+H 1.00E+13 0.00 0.0 ! EST JetSurF 2.0

C4H7+H = CH3+aC3H5 2.00E+21 -2.00 11000.0 ! Estimated USC Mech V2.0

C4H7+H = C4H6+H2 1.80E+12 0.00 0.0 ! = nC3H7+H USC Mech V2.0

C4H7+CH3 = C4H6+CH4 1.10E+13 0.00 0.0 ! = nC3H7+CH3 USC Mech V2.0

! reactions of C4H7-2 CH3CCHCH3

C4H7-2 = SAXC4H7 2.00E+12 0.0 47000 ! 2007 Gueniche et al./10

C4H7-2 = CH3+aC3H4 2.00E+12 0.0 32500 ! 2007 Gueniche et al./10

C4H7-2 = C4H7 3.30E+08 1.0 43300 ! 2007 Gueniche et al./10

C4H612+H = C4H7-2 1.30E+12 0.0 3200 ! 2007 Gueniche et al./10

CH3CCHCH3=pC3H4+CH3 2.00E+12 0.0 31500 ! 2007 Gueniche et al./10

C4H7-2+H=pC3H4+CH4 3.00E+13 0.0 0.0 ! EST

! reactions of iC4H7 iC4H7-1

iC4H7=aC3H4+CH3 1.00E+12 0.0 51000 ! 2009 Yasunaga et al. /10

iC4H7+H=aC3H4+CH4 6.31E+13 0.0 0.0 ! 2009 Yasunaga et al.

iC4H7=SAXC4H7 6.00E+13 0. 70000 ! 2012 Zhang et al.

iC4H7+H=SAXC4H7+H 1.47E+13 0.26 4103 ! Ref aC3H4+H=pC3H4+H

iC4H7+H = aC3H5+CH3 2.20E+51 -9.98 37730.0 ! =(aC3H5+H) TS5 0.1 atm USC Mech V2.0

iC4H7+H = CH3CCH2+CH3 2.20E+51 -9.98 37730.0 ! =(aC3H5+H) TS5 0.1 atm USC Mech V2.0

iC4H7-1=pC3H4+CH3 1.30E+14 0.0 37000 ! 2009 Yasunaga et al.

iC4H7-1=iC4H7 5.00E+12 0.0 36000 ! 2009 Yasunaga et al.

!reactions of C4H8-1

aC3H5+CH3(+M)=C4H8-1(+M) 1.00E+14 -0.32 -262. ! 1991 TSA

LOW /3.51E+60 -12.97 6000./

TROE / 0.896 60000 1606 6118/

H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/

C2H5+C2H3(+M) = C4H8-1(+M) 1.50E+13 0.00 0.0 ! 1986 TSA/HAM

LOW / 1.55E+56 -11.79 8984.5/

TROE / 0.198 2277.9 60000.0 5723.2 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C4H7+H(+M) = C4H8-1(+M) 3.60E+13 0.00 0.0 ! = nC3H7+H USC Mech V2.0

LOW / 3.01E+48 -9.32 5833.6/

TROE / 0.498 1314.0 1314.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

SAXC4H7+H(+M) = C4H8-1(+M) 2.00E+14 0.00 0.0 ! (ac3H5+H) JetSurF 2.0

LOW / 2.66E+60 -12.00 5967.8 / ! 2*(aC3H5+H)

H2/2/ CH4/2/ C2H6/3/

C4H8-1+H=C4H8-2+H 5.00E+14 -0.26 7600.0 ! Refa: pC3H4+H = aC3H4+H in USC Mech V2.0

C4H7-2+H = C4H8-1 1.00E+13 0.0 0.0 ! EST 2012 Zhang et al.

C4H8-1+H = SAXC4H7+H2 1.30E+06 3.40 4471.0 ! (C3H8+H) USC Mech V2.0 !!ori n=2.40

C4H8-1+H = C4H7+H2 6.50E+05 2.5 6756 ! Refa C6H12-1E+H=P6XC6H11-1E+H2 in 2009 Kiefer et al.

C4H8-1+H = C4H7-2+H2 4.00E+05 2.50 9790.0 ! Refa to C3H6+H = CH3CCH2+H2

C4H8-1+H = C3H6+CH3 3.20E+22 -2.39 11180 ! 2012 Zhang et al.

C4H8-1+H = C2H4+C2H5 8.80E+16 -1.05 6461.0 ! Refa C3H6+H = C2H4+CH3

C4H8-1+CH3 = SAXC4H7+CH4 2.82E+00 3.60 7153 ! Refa C6H12-1E+CH3=S3XC6H11-1E+CH4 in 2009 Kiefer et al.

C4H8-1+CH3 = C4H7+CH4 4.50E-01 3.65 7153.0 ! (C3H8+CH3) USC Mech V2.0

! reactions of C4H8-2

CH3CHCH+CH3(+M) = C4H8-2(+M) 5.00E+13 0.0 0.00 ! Refa to C2H3+CH3(+M)=C3H6(+M)

LOW / 8.54E+58 -11.940 9769.80/

TROE / 0.175 1340.6 60000.0 10139.8/

H2/2/ CH4/2/ C2H6/3/ AR/0.7/C2H2/3.00/ C2H4/3.00/

SAXC4H7+H(+M) = C4H8-2(+M) 2.00E+14 0.00 0.0 ! (ac3H5+H) JetSurF 2.0

LOW / 2.66E+60 -12.00 5967.8 / ! 2*(aC3H5+H) H2/2/ CH4/2/ C2H6/3/

C4H8-2 = aC3H5+CH3 7.5E+65 -15.6 97300 ! 2012 Zhang et al.

C4H8-2+H = SAXC4H7+H2 3.16E+06 2.5 6756 ! 2012 Zhang et al.

C4H8-2+H=CH3CCHCH3+H2 1.32E+06 2.53 12240.0 ! EST

C4H8-2+H = C3H6+CH3 3.46E+17 -1.05 6461.0 ! 2012 Zhang et al.

C4H8-2+CH3 = SAXC4H7+CH4 4.40E+00 3.50 5675.0 ! Refa C3H6+CH3=aC3H5+CH3 x2 in USC Mech V2.0

C4H8-2+H = C4H7+H2 3.46E+05 2.50 2490.0 ! Refa (C3H6+H)*2 TS5 k(a) in USC Mech V2.0

C4H8-2+CH3 = C4H7+CH4 4.40E+00 3.50 5675.0 ! Refa (C3H6+CH3)*2 TS5 k(c) in USC Mech V2.0

!reactions of iC4H8

iC4H7+H(+M) = iC4H8(+M) 2.00E+14 0.00 0.0 !(=(aC3H5+H) TS5 600cm-1) USC Mech V2.0

LOW / 1.33E+60 -12.00 5967.8 /

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

CH3CCH2+CH3 (+M) = iC4H8(+M) 2.50E+13 0.00 0.0 ! Refa to C2H3+CH3 (+M) = C3H6(+M)

LOW / 4.270E+58 -11.940 9769.80/

TROE / 0.175 1340.6 60000.0 10139.8 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

iC4H8+H = iC4H7+H2 1.72E+14 0.0 8000 ! 2009 Yasunaga et al.

iC4H8+H = iC4H7-1+H2 1.20E+14 0.0 13000 ! 2009 Yasunaga et al.

! iC4H8+H = C3H6+CH3 8.80E+16 -1.05 6461.0 ! Refa C3H6+H = C2H4+CH3 (91TSA RRKM 0.1 atm) in USC Mech V2.0

iC4H8+CH3 = iC4H7+CH4 4.40E+00 3.50 5675.0 ! Refa C3H6+CH3=aC3H5+CH3 x2 in USC Mech V2.0

iC4H8+CH3 = iC4H7-1+CH4 2.00E+12 0.0 15000 ! 2009 Yasunaga et al.

iC4H8+H = C3H6+CH3 8.80E+16 -1.05 6461.0 !Refa USC Mech II

PLOG/ 0.1 8.80E+16 -1.05 6461.0 / !Refa USC Mech II

PLOG/ 1.0 8.00E+21 -2.39 11180.0 / !Refa USC Mech II

PLOG/ 10 3.30E+24 -3.04 15610.0 / !Refa USC Mech II

!reactions of pC4H9

pC4H9(+M) = C2H4+C2H5(+M) 1.00E+13 0.00 28366.4 ! EST

LOW / 7.10E-35 15.41 -600.0 /

TROE / -5.91 333.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C4H8-1+H(+M) = pC4H9(+M) 1.33E+13 0.00 3260.7 ! =(C3H6+H) TS5 600 cm-1 USC Mech V2.0

LOW / 6.26E+38 -6.66 7000.0 /

TROE / 1.000 1000.0 1310.0 48097.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

pC4H9+H = C2H5+C2H5 3.40E+18 -1.33 5386.0 ! =(nC3H7+H) TS3 0.1 atm USC Mech V2.0

pC4H9+CH3 = C4H8-1+CH4 1.10E+13 0.00 0.0 ! =(nC3H7+CH3) TS3 USC Mech V2.0

! reactions of sC4H9

C3H6+CH3(+M) = sC4H9(+M) 1.70E+11 0.00 7403.6 ! TS5 600cm-1 USC Mech V2.0

LOW / 2.31E+28 -4.27 1831.0 /

TROE / 0.565 60000.0 534.2 3007.2 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C4H8-1+H(+M) = sC4H9(+M) 1.33E+13 0.00 1559.8 ! =(C3H6+H) TS5 600 cm-1 USC Mech V2.0

LOW / 8.70E+42 -7.50 4721.8 /

TROE / 1.000 1000.0 645.4 6844.3 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C4H8-2+H(+M) = sC4H9(+M) 1.33E+13 0.00 1559.8 ! =(C3H6+H=iC3H7) TS5 600cm-1 USC Mech V2.0

LOW / 8.70E+42 -7.50 4721.8 /

TROE / 1.000 1000.0 645.4 6844.3 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

sC4H9+H = C4H8-1+H2 3.20E+12 0.00 0.0 ! =(iC3H7+H) TS3 USC Mech V2.0

sC4H9+H = C4H8-2+H2 2.10E+12 0.00 0.0 ! =(iC3H7+H)*2/3 TS3 USC Mech V2.0

sC4H9+CH3 = CH4+C4H8-1 2.20E+14 -0.68 0.0 ! =(iC3H7+CH3) TS3 USC Mech V2.0

sC4H9+CH3 = CH4+C4H8-2 1.50E+14 -0.68 0.0 ! =(iC3H7+CH3)*2/3 TS3 USC Mech V2.0

!reactions of iC4H9

C3H6+CH3(+M) = iC4H9(+M) 9.60E+10 0.00 8003.6 ! TS5 600cm-1 USC Mech V2.0

LOW / 1.30E+28 -4.27 2431.1 /

TROE / 0.565 60000.0 534.2 3007.2 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

iC4H8+H(+M) = iC4H9(+M) 1.33E+13 0.00 3260.7 ! =(C3H6+H=nC3H7) TS5 600 cm-1 USC Mech V2.0

LOW / 6.26E+38 -6.66 7000.0 /

TROE / 1.000 1000 1310.0 48097.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

iC4H9+H = iC3H7+CH3 1.10E+32 -5.04 16760.0 ! TS4 eq 0.1 atm USC Mech V2.0

iC4H9+H = iC4H8+H2 9.00E+11 0.00 0.0 ! TS4 USC Mech V2.0

iC4H9+CH3 = iC4H8+CH4 6.00E+12 -0.32 0.0 ! TS4 USC Mech V2.0

! reactions of tC4H9

tC4H9(+M) = iC4H8+H(+M) 8.30E+13 0.00 38150.4 ! TS4 600cm-1 USC Mech V2.0

LOW / 1.90E+41 -7.36 36631.7/

TROE / 0.293 649.0 60000 3425.9 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

tC4H9+H = iC3H7+CH3 2.80E+34 -5.69 20500.0 ! TS4 eq 0.1 atm USC Mech V2.0

tC4H9+H = iC4H8+H2 5.42E+12 0.00 0.0 ! TS4 USC Mech V2.0

tC4H9+CH3 = iC4H8+CH4 3.80E+15 -1.00 0.0 ! TS4 USC Mech V2.0

! reactions of C5H7

aC3H4+C2H3 = P1XCH2C4H5-13E 1.23E+35 -7.76 9930.0 ! Refa to C2H4+C2H3 = C4H7

PLOG / 0.039 6.15E+34 -7.76 9930.0 /

PLOG / 0.1 1.23E+35 -7.76 9930.0 /

PLOG / 1.0 7.93E+38 -8.47 14220.0/

PLOG / 10 2.99E+36 -7.40 15480.0/ !

C2H2 + CH3CCH2 = S4XC4H4-13E2M 1.10E+31 -7.14 5600. ! Refa to C2H3 + C2H2 = nC4H5

PLOG / 0.013 1.10E+31 -7.14 5600. /

PLOG / 0.026 1.10E+32 -7.33 6200. /

PLOG / 0.118 2.40E+31 -6.95 5600. /

PLOG / 1.0 9.30E+38 -8.76 12000./

PLOG / 10.0 8.10E+37 -8.09 13400./

C2H3 + pC3H4 = T4XC5H7-13E 1.10E+31 -7.14 5600. ! Refa to C2H3 + C2H2 = nC4H5

PLOG / 0.013 1.10E+31 -7.14 5600. /

PLOG / 0.026 1.10E+32 -7.33 6200. /

PLOG / 0.118 2.40E+31 -6.95 5600. /

PLOG / 1.0 9.30E+38 -8.76 12000./

PLOG / 10.0 8.10E+37 -8.09 13400./

C4H4+CH3 = S1XC4H4-13E2M 1.40E+32 -7.14 10000.0 ! Refa to C2H2+CH3 = CH3CHCH

PLOG / 0.039 7.0E+31 -7.14 10000.0 /

PLOG / 0.1 1.40E+32 -7.14 10000.0 /

PLOG / 1.0 3.20E+35 -7.76 13300.0 /

PLOG / 10.0 2.40E+38 -8.21 17100.0 /

PLOG / 100.0 1.40E+39 -8.06 20200.0 /

C2H2 + CH3CHCH = T1XC5H7-13E 1.10E+31 -7.14 5600. ! Refa to C2H3 + C2H2 = nC4H5

PLOG / 0.013 1.10E+31 -7.14 5600. /

PLOG / 0.026 1.10E+32 -7.33 6200. /

PLOG / 0.118 2.40E+31 -6.95 5600. /

PLOG / 1.0 9.30E+38 -8.76 12000./

PLOG / 10.0 8.10E+37 -8.09 13400./

! reactions of C5H8

C5H8-13E+H = C2H4+CH3CHCH 1.46E+30 -4.34 21647.0 ! =(C4H6+H) JetSurF 2.0

C5H8-13E+H = C4H6-2+CH3 2.00E+12 0.0 7000. ! =(C4H6+H) JetSurF 2.0

C5H8-13E+H = C4H612+CH3 2.00E+12 0.0 7000. ! =(C4H6+H) JetSurF 2.0

C5H8-13E+H = lC5H7+H2 1.73E+05 2.50 2490.0 ! (=C3H6+H) JetSurF 2.0

C5H8-13E+CH3 = lC5H7+CH4 2.20E+00 3.50 5675.0 ! =(C3H6+CH3) JetSurF 2.0

C5H8-12E = C5H8-13E 1.1E+13 0.00 67000.0 !

PLOG / 0.039 1.1E+13 0.00 67000.0 / ! /20 EST

PLOG / 1.0 2.20E+14 0.00 67000.0/ ! JetSurF 2.0

C5H8-12E = C2H4+pC3H4 3.30E+11 0.00 58100.0 !

PLOG / 0.039 3.30E+11 0.00 58100.0 / ! /20 EST

PLOG / 1.0 6.60E+12 0.00 58100.0/ ! JetSurF 2.0

nC4H5+CH3 = C5H8-13E 3.60E+12 0.00 0.0 !

PLOG / 0.039 3.60E+12 0.00 0.0 / ! /20 EST

PLOG / 1.0 7.23E+13 0.00 0.0/ ! 04/LAU-FAR JetSurF 2.0

C5H8-14E+H = aC3H5+C2H4 1.60E+22 -2.39 11180.0 ! = C3H6+H JetSurF 2.0

C5H8-14E+H = lC5H7+H2 1.15E+05 2.50 2490.0 ! (=C3H6+H) JetSurF 2.0

C5H8-14E+H = C4H6+CH3 2.00E+12 0.0 7000. ! =(C4H6+H) JetSurF 2.0

C5H8-14E+CH3 = lC5H7+CH4 1.47E+00 3.50 5675.0 ! =(C3H6+CH3) JetSurF 2.0

C4H5-13E2M+H = C3H6+C2H3 1.46E+30 -4.34 21647.0 ! =(C4H6+H) JetSurF 2.0

C4H5-13E2M+H = CH3CCH2+C2H4 1.46E+30 -4.34 21647.0 ! =(C4H6+H)

C4H5-13E2M+H = C4H6+CH3 8.00E+21 -1.39 11180.0 ! 1991 TSA RRKM 1 atm JetSurF 2.0 ori n -2.39

C4H5-13E2M+H = P1XCH2C4H5-13E+H2 1.20E+06 2.54 6760.0 ! 1989 TSA (=iC4H8+H) JetSurF 2.0

C4H5-13E2M+CH3 = P1XCH2C4H5-13E+CH4 2.20E+00 3.50 5675.0 ! =(C3H6+CH3) JetSurF 2.0

CH3+iC4H5 = C4H5-13E2M 1.00E+12 0.00 0.0 !

PLOG / 0.039 1.00E+12 0.00 0.0 / ! /20 EST

PLOG / 1.0 2.00E+13 0.0 0.0/ ! JetSurF 2.0

P1XCH2C4H5-13E+H(+M) = C4H5-13E2M(+M) 2.00E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M)

LOW / 1.33E+60 -12.00 5967.8/

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

! reactions of C5H9

S3XC5H9-1E(+M) = C4H6+CH3(+M) 3.39E+11 0.66 32262.9 ! Refa S3XC6H11-1E(+M) = C4H6+C2H5(+M) in JetSurF 2.0

LOW / 4.00E-42 18.05 -602.6 /

TROE / -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S3XC5H9-1E(+M) = C5H8-13E+H(+M) 4.70E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M)

LOW / 4.6E-37 15.37 -603.1/

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

P5XC5H9-1E+H = CH3+C4H7 2.00E+21 -2.00 11000.0 ! Estimated JetSurF 2.0

P5XC5H9-1E(+M) = C2H4+aC3H5(+M) 4.57E+12 0.13 24386.4 ! Refa S5XC6H11-1E(+M) = C3H6+aC3H5(+M)

```
LOW / 2.50E-31 14.57 -578.8 /
TROE / -13.17 268 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C5H8-14E+H(+M) = P5XC5H9-1E(+M) 1.33E+13 0.00 3260.7 ! Refa to C3H6+H(+M) = nC3H7(+M)
LOW / 6.26E+38 -6.66 7000.0/
TROE / 1.000 1000.0 1310.0 48097.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S4XC5H9-1E = C5H8-13E+H 1.27E+24 -4.75 23777 ! Refa to C4H7 = C4H6+H
PLOG / 0.033 1.27E+24 -4.75 23777/
PLOG / 0.066 1.38E+26 -5.221 25729/
PLOG / 0.132 1.75E+28 -5.709 27764/
PLOG / 0.197 3.16E+29 -6.003 28985/
PLOG / 0.263 2.69E+30 -6.222 29890/
PLOG / 1.0 2.48E+53 -12.30 52000/
PLOG / 10 1.85E+48 -10.50 51770/
C3H6+C2H3 = S4XC5H9-1E 1.23E+35 -7.76 9930.0 ! Refa to C2H4+C2H3=C4H7
PLOG / 0.033 6.15E+34 -7.76 9930 /
PLOG / 0.1 1.23E+35 -7.76 9930 /
PLOG / 1.0 7.93E+38 -8.47 14220/
PLOG / 10 2.99E+36 -7.40 15480/
S4XC5H9-2E(+M) = C5H8-13E+H(+M) 4.70E+08 1.32 44697.6 ! Refa to SAXC4H7 = C4H6 + H
LOW / 4.6E-37 15.37 -603.1/
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
P5XC5H9-2E = C5H8-13E+H 1.27E+24 -4.75 23777 ! Refa to C4H7 = C4H6+H
PLOG / 0.033 1.27E+24 -4.75 23777/
PLOG / 0.066 1.38E+26 -5.221 25729/
PLOG / 0.132 1.75E+28 -5.709 27764/
PLOG / 0.197 3.16E+29 -6.003 28985/
PLOG / 0.263 2.69E+30 -6.222 29890/
PLOG / 1.0 2.48E+53 -12.30 52000/
PLOG / 10 1.85E+48 -10.50 51770/
CH3CHCH+C2H4 = P5XC5H9-2E 1.23E+35 -7.76 9930 ! Refa to C2H4+C2H3 = C4H7
PLOG / 0.033 6.15E+34 -7.76 9930 /
PLOG / 0.1 1.23E+35 -7.76 9930 /
PLOG / 1.0 7.93E+38 -8.47 14220/
PLOG / 10 2.99E+36 -7.40 15480/
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C4H6+CH3(+M) = P4XC4H6-1E3M(+M) 9.60E+10 0.00 8003.6 ! Refa to C3H6+CH3(+M) = iC4H9(+M)
LOW / 1.30E+28 -4.27 2431.1 /
TROE / 0.565 60000.0 534.2 3007.2 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
P4XC4H6-1E3M = C4H5-13E2M+H 6.35E+23 -4.75 23777 ! Refa to C4H7 = C4H6+H /2
PLOG / 0.033 6.35E+23 -4.75 23777/
PLOG / 0.066 6.90E+25 -5.221 25729/
PLOG / 0.132 8.75E+27 -5.709 27764/
PLOG / 0.197 1.58E+29 -6.003 28985/
PLOG / 0.263 1.35E+30 -6.222 29890/
PLOG / 1.0 1.24E+53 -12.30 52000/
PLOG / 10 9.25E+47 -10.50 51770/
C2H3+C3H6 = P4XC4H6-1E3M 1.23E+35 -7.76 9930 ! Refa to C2H4+C2H3 = C4H7
PLOG / 0.033 6.15E+34 -7.76 9930/
PLOG / 0.1 1.23E+35 -7.76 9930/
PLOG / 1.0 7.93E+38 -8.47 14220/
PLOG / 10 2.99E+36 -7.40 15480/
P4XC4H6-1E2M = C4H5-13E2M+H 1.27E+24 -4.75 23777 ! Refa to C4H7 = C4H6+H
PLOG / 0.033 1.27E+24 -4.75 23777/
PLOG / 0.066 1.38E+26 -5.221 25729/
PLOG / 0.132 1.75E+28 -5.709 27764/
PLOG / 0.197 3.16E+29 -6.003 28985/
PLOG / 0.263 2.69E+30 -6.222 29890/
PLOG / 1.0 2.48E+53 -12.30 52000/
PLOG / 10 1.85E+48 -10.50 51770/
CH3CCH2+C2H4 = P4XC4H6-1E2M 1.23E+35 -7.76 9930.0 ! Refa to C2H4+C2H3 = C4H7
PLOG / 0.033 6.15E+34 -7.76 9930/
PLOG / 0.1 1.23E+35 -7.76 9930/
PLOG / 1.0 7.93E+38 -8.47 14220/
PLOG / 10 2.99E+36 -7.40 15480/
! reactions of C5H10-1E
S4XC5H9-1E+H(+M) = C5H10-1E(+M) 2.40E+13 0.00 0.0 ! = iC3H7+H
LOW / 1.70E+58 -12.08 11263.7 /
TROE / 0.649 1213.1 1213.1 13369.7 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
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```
S3XC5H9-1E+H(+M)=C5H10-1E(+M) 2.00E+14 0.00 0.0 ! (aC3H5+H)
LOW / 1.33E+60 -12.00 5967.8 /
TROE / 0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
P5XC5H9-1E+H(+M) = C5H10-1E(+M) 3.60E+13 0.00 0.0 ! =nC3H7+H JetSurF 2.0
LOW / 3.01E+48 -9.32 5833.6 /
TROE / 0.498 1314.0 1314.0 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C5H10-1E=aC3H5+C2H5 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7 !
PLOG / 0.039 1.07E+80 -19.33 95177/
PLOG / 0.066 2.50E+68 -16.040 86832/
PLOG / 0.132 1.480E+59 -13.261 82596/
PLOG / 0.197 2.43E+61 -13.999 82637/
PLOG / 0.263 3.75E+59 -13.427 82179/
PLOG / 1.0E+5 1.46E+16 0.00 69120/
C5H10-1E=C4H7+CH3 2.7E+80 -1.93E+01 1.07E+05 ! Refa to C6H12-1E=C4H7+C2H5
PLOG / 0.033 2.7E+80 -19.331 107015/
PLOG / 0.066 6.27E+68 -16.040 98670/
PLOG / 0.132 3.70E+59 -13.261 94434/
PLOG / 0.197 6.08E+61 -13.999 94475/
PLOG / 0.263 9.38E+59 -13.427 94017/
PLOG / 1.0E+5 1.46E+16 0 81020/
C5H10-1E = C3H6+C2H4 8.0E+05 1.81 53454 !
PLOG / 0.039 8.0E+05 1.81 53454/ ! 1.62E+06 /20 EST
PLOG / 1 1.62E+06 1.81 53454/ ! 08/TSAwip JetSurF 2.0
C5H10-1E+H = S3XC5H9-1E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571
C5H10-1E+CH3 = S3XC5H9-1E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
C5H10-1E+H = S4XC5H9-1E+H2 1.3E06 2.4 4471 ! secondary LLNL-MI-407571
C5H10-1E+CH3 = S4XC5H9-1E+CH4 1.51 3.46 5481 ! secondary LLNL-MI-407571
C5H10-1E+H = P5XC5H9-1E+H2 6.651E05 2.54 6756 ! primary LLNL-MI-407571
C5H10-1E+CH3 = P5XC5H9-1E+CH4 4.521E-1 3.65 7154 ! primary LLNL-MI-407571
! reactions of C5H10-2E
SAXC4H7+CH3(+M)=C5H10-2E(+M) 1.00E+14 -0.32 -262. ! Refa to aC3H5+CH3=C4H8-1
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LOW /3.51E+60 -12.97 6000./
TROE / 0.896 60000 1606 6118/
H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/
C2H5+CH3CHCH(+M) = C5H10-2E(+M) 1.50E+13 0.00 0.0 ! Refa to C2H5+C2H3=C4H8-1
LOW /1.55E+56 -11.79 8984.5/
TROE /0.198 2277.9 60000.0 5723.2 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
P5XC5H9-2E+H(+M) = C5H10-2E(+M) 3.60E+13 0.00 0.0 ! Refa to C4H7+H = C4H8-1
LOW / 3.01E+48 -9.32 5833.6 /
TROE / 0.498 1314.0 1314.0 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S4XC5H9-2E+H(+M) = C5H10-2E(+M) 2.00E+14 0.00 0.0 ! Refa to SAXC4H7+H = C4H8-1
LOW / 2.66E+60 -12.00 5967.8 /
H2/2/ CH4/2/ C2H6/3/
S3XC5H9-1E+H(+M) = C5H10-2E(+M) 2.00E+14 0.00 0.0 ! Refa to aC3H5+H = C3H6
LOW / 1.33E+60 -12.00 5967.8 /
TROE/ 0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C5H10-2E+H = S3XC5H9-1E+H2 1.73E5 2.5 2492 ! allylp LLNL-MI-407571
C5H10-2E+CH3 = S3XC5H9-1E+CH4 2.2098 3.5 5675 ! allylp LLNL-MI-407571
C5H10-2E+H = S4XC5H9-2E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571
C5H10-2E+CH3 = S4XC5H9-2E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
C5H10-2E+H = P5XC5H9-2E+H2 6.651E05 2.54 6756 ! primary LLNL-MI-407571
C5H10-2E+CH3 = P5XC5H9-2E+CH4 4.521E-1 3.65 7154 ! primary LLNL-MI-407571
! reactions of C5H11
P1XC5H11(+M) = C2H4+nC3H7(+M) 1.00E+13 0.00 28366.4 ! 1998 TSA JetSurF 2.0
LOW / 7.10E-35 15.411 -600.0/
TROE / -5.91 333.0 28.0 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
P1XC5H11(+M) = S2XC5H11(+M) 1.00E+12 0.00 22453.1 ! 1998 TSA JetSurF 1.1
LOW / 2.00E-26 12.833 -600.7/
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TROE / -10.14 307.0 28.0 5000000 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C5H10-1E+H(+M) = P1XC5H11(+M) 1.33E+13 0.00 3260.7 ! Refa C3H6+H(+M) = nC3H7(+M)
LOW / 6.26E+38 -6.66 7000.0 /
TROE / 1.000 1000.0 1310.0 48097.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
P1XC5H11+H = nC3H7+C2H5 3.40E+18 -1.33 5386.0 ! =(nC3H7+H) 0.1 atm JetSurF 2.0
P1XC5H11+H = C5H10-1E+H2 1.80E+12 0.00 0.0 ! =(nC3H7+H) JetSurF 2.0
P1XC5H11+CH3 = C5H10-1E+CH4 1.10E+13 0.00 0.0 ! =(nC3H7+CH3) JetSurF 2.0
S2XC5H11(+M) = C3H6+C2H5(+M) 8.00E+12 0.00 27392.8 ! 1998 TSA JetSurF 2.0
LOW / 3.70E-33 14.91 -600.0 /
TROE / -6.53 333.0 28.0 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C5H10-1E+H(+M) = S2XC5H11(+M) 1.33E+13 0.00 1559.8 ! Refa C3H6+H(+M) = iC3H7(+M) USC Mech II
LOW / 8.70E+42 -7.50 4721.8/
TROE / 1.000 1000.0 645.4 6844.3 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S2XC5H11+H = nC3H7+C2H5 5.90E+23 -2.81 10009.0 ! =(iC3H7+H) JetSurF 2.0
S2XC5H11+H = C5H10-1E+H2 3.20E+12 0.00 0.0 ! =(iC3H7+H) JetSurF 2.0
S2XC5H11+CH3 = CH4+C5H10-1E 2.20E+14 -0.68 0.0 ! =(iC3H7+CH3) JetSurF 2.0
S3XC5H11(+M) = C4H8-1+CH3(+M) 1.80E+13 0.00 29348.0 ! 1998 TSA JetSurF 2.0
LOW / 4.00E-39 16.782 -600.4/
TROE / -7.03 314.0 28.0 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
! C6H10 C6H9 C6H8 reactions
lC5H7(+M)+CH3 = C6H10-13E(+M) 1.00E+14 -0.32 -262.3 ! 1991 TSA JetSurF 2.0
LOW / 3.91E+60 -12.81 6250.0 /
TROE / 0.104 1606.0 60000.0 6118.4 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
```

C6H10-13E+H = C4H8-1+C2H3 1.46E+30 -4.34 21647.0 ! =(C4H6+H) JetSurF 2.0

C6H10-13E + H = S5XC6H9-13E + H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571

C6H10-13E + CH3 = S5XC6H9-13E + CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C6H10-15E = aC3H5+aC3H5 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

C6H10-15E + H = S3XC6H9-15E + H2 6.752E05 2.36 207 ! (ax4) allyls LLNL-MI-407571

C6H10-15E + CH3 = S3XC6H9-15E + CH4 7.38 3.31 4002 ! (ax4) allyls LLNL-MI-407571

S5XC6H9-13E(+M) = C6H8-135E+H(+M) 4.70E+08 1.32 44697.6 ! Refa to SAXC4H7

LOW / 4.6E-37 15.37 -603.1 /

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

S3XC6H9-15E = C6H8-135E+H 1.27E+24 -4.75 23777 ! Refa to C4H7 = C4H6+H

PLOG / 0.033 1.27E+24 -4.75 23777/

PLOG / 0.066 1.38E+26 -5.221 25729/

PLOG / 0.132 1.75E+28 -5.709 27764/

PLOG / 0.197 3.16E+29 -6.003 28985/

PLOG / 0.263 2.69E+30 -6.222 29890/

PLOG / 1.0 2.48E+53 -12.30 52000/

PLOG / 10 1.85E+48 -10.50 51770/

C4H6+C2H3 = S3XC6H9-15E 1.23E+35 -7.76 9930 ! Refa to C2H4+C2H3 = C4H7

PLOG / 0.039 6.15E+34 -7.76 9930/

PLOG / 0.1 1.23E+35 -7.76 9930/

PLOG / 1.0 7.93E+38 -8.47 14220/

PLOG / 10 2.99E+36 -7.40 15480/

C2H3 + nC4H5 = C6H8-135E 7.00E+57 -13.82 17629. ! Refa to C2H3+C2H3=C4H6

PLOG / 0.026 7.00E+57 -13.82 17629/

PLOG / 0.118 1.50E+52 -11.97 16056/

PLOG / 1.0 1.50E+42 -8.84 12483/

P6XC6H9-13E = C6H8-135E+H 1.27E+24 -4.75 23777 ! Refa to C4H7 = C4H6+H

PLOG / 0.033 1.27E+24 -4.75 23777/

PLOG / 0.066 1.38E+26 -5.221 25729/

PLOG / 0.132 1.75E+28 -5.709 27764/

PLOG / 0.197 3.16E+29 -6.003 28985/

PLOG / 0.263 2.69E+30 -6.222 29890/

PLOG / 1.0 2.48E+53 -12.30 52000/

PLOG / 10 1.85E+48 -10.50 51770/

C2H4+nC4H5=P6XC6H9-13E 1.23E+35 -7.76 9930 ! Refa to C2H4+C2H3 = C4H7

PLOG / 0.039 6.15E+34 -7.76 9930/

PLOG / 0.1 1.23E+35 -7.76 9930/

PLOG / 1.0 7.93E+38 -8.47 14220/

PLOG / 10 2.99E+36 -7.40 15480/

C6H8-135E+H = C2H4+nC4H5 1.46E+30 -4.34 21647 ! Refa to C4H6+H = C2H4+C2H3

C6H8-135E+H = C2H3+C4H6 1.46E+30 -4.34 21647 ! Refa to C4H6+H = C2H4+C2H3

! cC6H10 cC6H9 cC6H8 reactions

cC6H10 = C4H6+C2H4 5.0E+78 -18.94 98386 ! EST

PLOG / 0.039 5.0E+78 -18.94 98386/

PLOG / 0.197 2.60E+70 -16.36 95510/

PLOG / 1.0 3.81E+25 -3.58 64034/

PLOG / 1.0E+5 8.31E+13 0.387 64116/

S2XcC6H9-1E+H(+M) = cC6H10(+M) 2.66E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *4/3

LOW / 1.77E+60 -12.00 5967.8 /

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

cC6H10+H = S2XcC6H9-1E+H2 6.752E05 2.36 207 ! (ax4) allyls LLNL-MI-407571

cC6H10 + CH3 = S2XcC6H9-1E+CH4 7.38 3.31 4002 ! (ax4) allyls LLNL-MI-407571

cC6H10+H=S3XcC6H9-1E+H2 1.3E06 2.4 4471 ! secondary LLNL-MI-407571

cC6H10+CH3=S3XcC6H9-1E+CH4 1.51 3.46 5481 ! secondary LLNL-MI-407571

S2XcC6H9-1E = cC6H8-13E+H 2.67E+12 0.71 49792.2 ! JetSurF 2.0

PLOG / 0.039 1.62E+57 -13.03 66036/ ! 2011 Li et al.

PLOG / 1.0 2.67E+12 0.71 49792.2/ ! JetSurF 2.0

S2XcC6H9-1E=P6XC6H9-13E 1.30E+13 0.00 35900 ! 2003 Dayma et al.

PLOG / 0.039 5.36E+50 -11.92 48276/ ! 2011 Li et al.

PLOG / 1.0 1.30E+13 0.00 35900/ ! 2003 Dayma et al.

S2XcC6H9-1E+H = cC6H8-13E+H2 1.80E+13 0.00 0.0 ! Refa to SAXC4H7+H

S3XcC6H9-1E=S3XC6H9-15E 1.1E12 0.53 16166 ! Gong 2012

S3XcC6H9-1E = cC6H8-14E+H 2.14E+11 0.92 46792 ! Gong 2012, Refer to S3XcC6H9-1E = cC6H8-13E+H

S3XcC6H9-1E = cC6H8-13E+H 9.12E9 0.88 34639 ! Gong 2012, P6XC6H9-13E = C6H8-135E+H

cC6H8-13E+H = S1XcC6H7-24E+H2 6.752E05 2.36 207 ! (ax4) allyls LLNL-MI-407571

cC6H8-13E + CH3 = S1XcC6H7-24E+CH4 7.38 3.31 4002 ! (ax4) allyls LLNL-MI-407571

S1XcC6H7-24E=A1+H 6.76E+11 0.78 30230 !

PLOG / 0.039 3.40E+10 0.78 30230/ ! /20 EST

PLOG / 1.0 6.76E+11 0.78 30230/ ! JetSurF 2.0

S1XcC6H7-24E+H = A1+H2 1.80E+13 0.00 0.0 ! Refa to SAXC4H7+H

! C6H11 reactions

P6XC6H11-1E(+M) = C4H7+C2H4(+M) 3.98E+12 0.12 27571.6 ! JetSurF 2.0

LOW / 3.30E-43 18.35 -602.5 /

TROE / -13.87 227 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C6H10-15E+H(+M) = P6XC6H11-1E(+M) 1.33E+13 0.00 3260.7 ! Refa to C3H6+H(+M) = nC3H7(+M)

LOW / 6.26E+38 -6.66 7000.0/

TROE / 1.000 1000.0 1310.0 48097.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

P6XC6H11-1E(+M) = S3XC6H11-1E(+M) 1.55E+02 2.83 15566.2 ! JetSurF 2.0

LOW / 1.50E-30 14.56 -602.4 /

TROE / -13.59 214 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S3XC6H11-1E(+M) = C4H6+C2H5(+M) 3.39E+11 0.66 32262.9 ! JetSurF 2.0

LOW / 4.00E-42 18.05 -602.6 /

TROE / -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

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S3XC6H11-1E(+M) = C6H10-13E+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7 = C4H6 + H *2/3
LOW / 3.07E-37 15.37 -603.1/
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
S3XC6H11-1E+H=C6H10-13E+H2 1.60E+12 0.00 0.0 ! Refa to iC3H7+H /2
S3XC6H11-1E+CH3=C6H10-13E+CH4 4.7E+10 0.68 0.0 ! Refa to iC3H7+CH3 /2
S5XC6H11-1E(+M) = C3H6+aC3H5(+M) 4.57E+12 0.13 24386.4 ! JetSurF 2.0
LOW / 2.50E-31 14.57 -578.8 /
TROE / -13.17 268 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C6H10-15E+H(+M) = S5XC6H11-1E(+M) 1.33E+13 0.00 1559.8 ! Refa to C4H8-1+H(+M) = sC4H9(+M)
LOW / 8.70E+42 -7.50 4721.8 /
TROE / 1.000 1000.0 645.4 6844.3 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S4XC6H11-1E(+M) = C5H8-14E+CH3(+M) 8.13E+10 0.78 29648.0 ! 2007 TSA JetSurF 2.0
LOW / 4.00E-39 16.782 -600.4 /
TROE / -7.03 314.0 28.0 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S4XC6H11-1E = C6H10-13E+H 1.27E+24 -4.75 23777 ! Refa to C4H7 = C4H6+H
PLOG / 0.033 1.27E+24 -4.75 23777/
PLOG / 0.066 1.38E+26 -5.221 25729/
PLOG / 0.132 1.75E+28 -5.709 27764/
PLOG / 0.197 3.16E+29 -6.003 28985/
PLOG / 0.263 2.69E+30 -6.222 29890/
PLOG / 1.0 2.48E+53 -12.30 52000/
PLOG / 10 1.85E+48 -10.50 51770/
S4XC6H11-1E+H = nC3H7+aC3H5 2.00E+21 -2.00 11000 ! Refa to C4H7+H
S4XC6H11-1E+H = C6H10-13E+H2 1.80E+12 0.00 0.0 ! Refa to C4H7+H
S4XC6H11-1E+CH3 = C6H10-13E+CH4 1.10E+13 0.00 0.0 ! Refa to C4H7+CH3
P1XCH2cC5H9=P6XC6H11-1E 8.92E+18 -2.94 19897 ! Refa to PXCH2cC6H11=P7XC7H13-1E
PLOG / 0.039 8.92E+18 -2.94 19897 /
PLOG / 0.197 6.83E+22 -3.82 23511 /
PLOG / 1.000 1.56E+29 -5.39 29211 /
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PLOG / 10.000 4.15E+37 -7.44 37753 /
PLOG / 100.000 1.92E+39 -7.58 42286 /
PLOG / 1.0E+5 2.53E+13 0.16 29785 /
! P1XCH2cC5H9=CH2cC5H8+H 8.14E+14 -2.42 21719 ! Refa to PXCH2cC6H11=CH2cC6H10+H
! PLOG / 0.039 8.14E+14 -2.42 21719 /
! PLOG / 0.197 1.23E+20 -3.61 26095 /
! PLOG / 1.000 1.18E+28 -5.58 32946 /
! PLOG / 10.000 1.31E+39 -8.28 43693 /
! PLOG / 100.000 4.67E+42 -8.87 50298 /
! PLOG / 1.0E+5 1.60E+11 0.59 35447 /
P1XCH2cC5H9(+M) = S3XcC5H81M(+M) 6.61E+01 2.85 21082.1 ! 08/TSAwip JetSurF 2.0
LOW / 1.10E-36 16.12 -602.5 /
TROE / -21.57 225 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S3XcC5H81M=P5XC5H8-1E4M 1.21E+18 -2.84 19903 ! Refa to S3XMCH=P6XC6H10-1E4M
PLOG / 0.039 1.21E+18 -2.84 19903 /
PLOG / 0.197 7.98E+21 -3.70 23365 /
PLOG / 1.000 2.52E+28 -5.31 28978 /
PLOG / 10.000 8.05E+37 -7.66 38033 /
PLOG / 100.000 6.13E+42 -8.70 44718 /
PLOG / 1.0E+5 1.68E+13 0.21 31241 /
S3XcC5H81M=S5XC6H11-1E 5.23E+18 -2.93 19555 ! Refa to S3XMCH=S6XC7H13-1E
PLOG / 0.039 5.23E+18 -2.93 19555 /
PLOG / 0.197 2.06E+22 -3.73 22876 /
PLOG / 1.000 3.29E+28 -5.27 28275 /
PLOG / 10.000 3.31E+37 -7.49 36918 /
PLOG / 100.000 8.80E+41 -8.42 43157 /
PLOG / 1.0E+5 2.55E+13 0.17 30061 /
P5XC5H8-1E4M(+M) = aC3H5+C3H6(+M) 5.37E+12 0.12 23947.3 ! 08/TSAwip JetSurF 2.0
LOW / 4.90E-31 14.54 -578.8 /
TROE / -11.90 267 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
! cC6H11 reactions
cC6H11=P6XC6H11-1E 1.26E+22 -3.85 22627 ! Refa to S4XMCH=P6XC6H10-1E5M
PLOG / 0.039 1.26E+22 -3.85 22627 /
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PLOG / 0.197 3.57E+26 -4.89 26638 /
PLOG / 1.000 2.59E+32 -6.32 32020 /
PLOG / 10.000 2.07E+41 -8.51 40814 /
PLOG / 100.000 5.79E+44 -9.15 46530 /
PLOG / 1.0E+5 3.87E+13 0.20 31782 /
cC6H11=cC6H10+H 8.38E+20 -3.63 23771 ! Refa to S4XMCH=MCH-3E+H
PLOG / 0.039 8.38E+20 -3.63 23771 /
PLOG / 0.197 8.32E+25 -4.80 28120 /
PLOG / 1.000 5.73E+32 -6.47 34206 /
PLOG / 10.000 1.37E+43 -9.02 44242 /
PLOG / 100.000 7.21E+47 -9.98 51272 /
PLOG / 1.0E+5 3.78E+12 0.63 34881 /
cC6H11+H = cC6H10+H2 3.60E+12 0.00 0.0 ! Refa to nC3H7+H *2
cC6H11+CH3 = cC6H10+CH4 2.20E+13 -0.32 0.0 ! Refa to nC3H7+CH3 *2
! C6H12-1E reactions
P6XC6H11-1E+H(+M) = C6H12-1E(+M) 3.60E+13 0.00 0.0 ! = nC3H7+H
LOW / 3.01E+48 -9.32 5833.6 /
TROE / 0.498 1314.0 1314.0 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S5XC6H11-1E+H(+M) = C6H12-1E(+M) 2.40E+13 0.00 0.0 ! = iC3H7+H
LOW / 1.70E+58 -12.08 11263.7/
TROE / 0.649 1213.1 1213.1 13369.7 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S4XC6H11-1E+H(+M) = C6H12-1E(+M) 2.40E+13 0.00 0.0 ! = iC3H7+H
LOW / 1.70E+58 -12.08 11263.7/
TROE / 0.649 1213.1 1213.1 13369.7 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S3XC6H11-1E+H(+M)=C6H12-1E(+M) 2.00E+14 0.00 0.0 ! = (aC3H5+H)
LOW / 1.33E+60 -12.00 5967.8/
TROE / 0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C6H12-1E=aC3H5+nC3H7 1.07E+80 -19.33 95177 !
PLOG / 0.039 1.07E+80 -19.33 95177/ ! 2009 Kiefer et al.
PLOG / 0.066 2.50E+68 -16.040 86832/ ! 2009 Kiefer et al.
PLOG / 0.132 1.480E+59 -13.261 82596/ ! 2009 Kiefer et al.
PLOG / 0.197 2.43E+61 -13.999 82637/ ! 2009 Kiefer et al.
PLOG / 0.263 3.75E+59 -13.427 82179/ ! 2009 Kiefer et al.
PLOG / 1.0E+5 1.46E+16 0.00 69120/ ! 2009 Kiefer et al.
C6H12-1E=C4H7+C2H5 2.7E+80 -19.331 107015
PLOG / 0.033 2.7E+80 -19.331 107015/ ! 2009 Kiefer et al.
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PLOG / 0.066 6.27E+68 -16.040 98670/ ! 2009 Kiefer et al.

PLOG / 0.132 3.70E+59 -13.261 94434/ ! 2009 Kiefer et al.

PLOG / 0.197 6.08E+61 -13.999 94475/ ! 2009 Kiefer et al.

PLOG / 0.263 9.38E+59 -13.427 94017/ ! 2009 Kiefer et al.

PLOG / 1.0E+5 1.46E+16 0.0 81020/ ! EST

C6H12-1E = C3H6+C3H6 7.08E+06 1.65 53752.0 !

PLOG / 0.039 3.54E+05 1.65 53752.0 / ! /20 EST

PLOG / 1.0 7.08E+06 1.65 53752.0 / ! JetSurF 2.0

C6H12-1E+H=S3XC6H11-1E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571

C6H12-1E+CH3=S3XC6H11-1E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C6H12-1E+H=S5XC6H11-1E+H2 1.3E06 2.4 4471 ! secondary LLNL-MI-407571

C6H12-1E+CH3=S5XC6H11-1E+CH4 1.51 3.46 5481 ! secondary LLNL-MI-407571

C6H12-1E+H=S4XC6H11-1E+H2 1.3E06 2.4 4471 ! secondary LLNL-MI-407571

C6H12-1E+CH3=S4XC6H11-1E+CH4 1.51 3.46 5481 ! secondary LLNL-MI-407571

C6H12-1E+H = P6XC6H11-1E+H2 6.651E05 2.54 6756 ! primary LLNL-MI-407571

C6H12-1E+CH3 = P6XC6H11-1E+CH4 4.521E-1 3.65 7154 ! primary LLNL-MI-407571

!cC6H12 reactions

cC6H11+H(+M)=cC6H12(+M) 4.80E+13 0.00 0.0 ! =(iC3H7+H) JetSurF 2.0

LOW / 1.70E+58 -12.08 11263.7/

TROE / 0.649 1213.1 1213.1 13369.7 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

cC6H12=C6H12-1E 1.33E+137 -34.70 162775 ! 2009 Kiefer et al.

PLOG / 0.039 1.33E+137 -34.70 162775/ ! /1.5

PLOG / 0.066 5.96E+139 -35.26 166598/ !

PLOG / 0.263 1.82E+143 -35.99 172904/ !

PLOG / 1.0E+5 8.76E+17 0.00 91940 / !

cC6H12+H=cC6H11+H2 2.70E+10 1.385 8229 ! 2009 Kiefer et al.

cC6H12+CH3=cC6H11+CH4 9.06E+00 3.46 5480 ! Refa to C3H8+CH3=iC3H7+CH4 *6

! CH2cC6H6-25E and CH2cC6H6-13E reactions

A1CH2+H(+M)=CH2cC6H6-13E(+M) 4.98E11 0.611 -436 ! oit 2007 Klippenstein

LOW / 1.34E52 -10.3 -3910 /

```
TROE / 0.01 1 -1300 50000/
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
A1CH2+H(+M)=CH2cC6H6-25E(+M) 6.44E12 0.245 -333 ! pit 2007 Klippenstein
LOW / 2.62E45 -8.59 -11590/
TROE / 0.025 1 -5000 50000/
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
CH2cC6H6-13E+H=A1CH2+H2 6.47E00 3.98 3394.0 ! Refa to A1CH3
CH2cC6H6-13E+CH3=A1CH2+CH4 3.160E+11 0.000 9500.00 ! Refa to A1CH3
CH2cC6H6-25E+H=A1CH2+H2 6.47E00 3.98 3394.0 ! Refa to A1CH3
CH2cC6H6-25E+CH3=A1CH2+CH4 3.160E+11 0.000 9500.00 ! Ref to A1CH3
! cC7H9 reactions
S5XMCH-13E(+M)=A1CH3+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) *2/3
LOW / 3.07E-37 15.37 -603.1 /
TROE /-51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
S6XMCH-13E(+M)=A1CH3+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) *2/3
LOW / 3.07E-37 15.37 -603.1 /
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
S3XMCH-15E(+M)=A1CH3+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3
LOW / 3.07E-37 15.37 -603.1 /
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
S4XMCH-15E(+M)=A1CH3+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3
LOW / 3.07E-37 15.37 -603.1 /
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
S2XMCH-35E(+M)=A1CH3+H(+M) 1.56E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) *1/3
LOW / 1.53E-37 15.37 -603.1 /
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
S2XMCH-35E=A1+CH3 4.24E+21 -3.89 22867 ! Refa to S2XMCH=cC6H10+CH3
PLOG / 0.039 4.24E+21 -3.89 22867 / !
PLOG / 0.197 2.58E+22 -3.86 24360 / !
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PLOG / 1.000 2.27E+28 -5.30 29571 / !
PLOG / 10.000 4.14E+38 -7.84 39088 / !
PLOG / 100.000 1.94E+45 -9.36 47105 / !
PLOG / 1.0E+5 6.35E+13 0.20 33524 / !
T1XMCH-35E(+M)=A1CH3+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) *2/3
LOW / 3.07E-37 15.37 -603.1 /
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
!T1XMCH-35E(+M)=CH2cC6H6-13E+H(+M) 4.70E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) ! 20131224 shielded
! LOW / 4.6E-37 15.37 -603.1 /
! TROE / -51.87 258 28 50000.0 /
! H2/2/ CH4/2/ C2H6/3/
CH2S4XcC6H7-5E(+M)=CH2cC6H6-13E+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) *2/3
LOW / 3.07E-37 15.37 -603.1 /
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
CH2S2XcC6H7-5E(+M)=CH2cC6H6-25E+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) *2/3
LOW / 3.07E-37 15.37 -603.1 /
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
! cC7H10 reactions
MCH-13E+H = S5XMCH-13E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571
MCH-13E+CH3= S5XMCH-13E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
S5XMCH-13E+H(+M)=MCH-13E(+M) 1.33E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M *2/3
LOW /0.89E+60 -12.00 5967.8/
TROE /0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S6XMCH-13E+H(+M)=MCH-13E(+M) 1.33E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M *2/3
LOW /0.89E+60 -12.00 5967.8/
TROE /0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
MCH-13E+H = S6XMCH-13E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571
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MCH-13E+CH3= S6XMCH-13E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

MCH-13E+H = CH2S4XcC6H7-5E+H2 1.73E5 2.5 2492 ! allylp LLNL-MI-407571

MCH-13E+CH3= CH2S4XcC6H7-5E+CH4 2.2098 3.5 5675 ! allylp LLNL-MI-407571

CH2S4XcC6H7-5E+H(+M)=MCH-13E(+M) 2.00E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M)

LOW /1.33E+60 -12.00 5967.8/

TROE /0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

MCH-15E+H = S3XMCH-15E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571

MCH-15E+CH3= S3XMCH-15E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

S3XMCH-15E+H(+M)=MCH-15E(+M) 1.33E+13 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/3

LOW /0.89E+59 -12.00 5967.8/

TROE /0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

MCH-15E+H = S4XMCH-15E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571

MCH-15E+CH3= S4XMCH-15E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

S4XMCH-15E+H(+M)=MCH-15E(+M) 1.33E+13 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/3

LOW /0.89E+59 -12.00 5967.8/

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

MCH-15E+H = CH2S2XcC6H7-5E+H2 1.73E5 2.5 2492 ! allylp LLNL-MI-407571

MCH-15E+CH3= CH2S2XcC6H7-5E+CH4 2.2098 3.5 5675 ! allylp LLNL-MI-407571

CH2S2XcC6H7-5E+H(+M)=MCH-15E(+M) 2.00E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M)

LOW /1.33E+60 -12.00 5967.8/

TROE /0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

MCH-35E+H = S2XMCH-35E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571

MCH-35E+CH3= S2XMCH-35E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

S2XMCH-35E+H(+M)=MCH-35E(+M) 1.33E+13 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/3

LOW / 0.89E+59 -12.00 5967.8 /

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

MCH-35E+H = T1XMCH-35E+H2 2.65E6 2.2 0.0 ! allylt LLNL-MI-407571

MCH-35E+CH3= T1XMCH-35E+CH4 4.613 3.1 2330 ! allylt LLNL-MI-407571

T1XMCH-35E+H(+M)=MCH-35E(+M) 0.67E+13 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *1/3

LOW / 0.44E+59 -12.00 5967.8 /

TROE/ 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S1XcC6H7-24E+CH3(+M)=MCH-35E(+M) 1.00E+14 -0.32 -262. ! Refa to aC3H5+CH3(+M)=C4H8-1(+M)

LOW / 3.51E+60 -12.97 6000./

TROE / 0.896 60000 1606 6118/

H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/

CH2cC6H8-2E+H = CH2S4XcC6H7-5E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571

CH2cC6H8-2E+CH3= CH2S4XcC6H7-5E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

CH2S4XcC6H7-5E+H(+M)=CH2cC6H8-2E(+M) 1.33E+13 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/3

LOW / 0.89E+59 -12.00 5967.8 /

TROE/ 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

CH2cC6H8-2E+H = CH2S2XcC6H7-5E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571

CH2cC6H8-2E+CH3= CH2S2XcC6H7-5E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

CH2S2XcC6H7-5E+H(+M)=CH2cC6H8-2E(+M) 1.33E+13 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/3

LOW / 0.89E+59 -12.00 5967.8 /

TROE/ 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

! C6H7-135E2M,C6H7-135E3M, C7H10-135E reactions

C6H7-135E2M+H = C4H6+CH3CCH2 1.46E+30 -4.34 21647 ! Refa to C4H6+H = C2H4+C2H3

C6H7-135E2M+H = S4XC4H4-13E2M+C2H4 1.46E+30 -4.34 21647 ! Refa to C4H6+H = C2H4+C2H3

C6H7-135E2M+H = C6H8-135E+CH3 8.80E+16 -1.05 6461.0 ! Refa to C3H6+H = C2H4+CH3

C6H7-135E2M+H = C3H6+nC4H5 1.46E+30 -4.34 21647 ! Refa to C4H6+H = C2H4+C2H3

C6H7-135E2M+H = C4H5-13E2M+C2H3 1.46E+30 -4.34 21647 ! Refa to C4H6+H = C2H4+C2H3

C6H7-135E3M+H = T4XC5H7-13E+C2H4 1.46E+30 -4.34 21647 ! Refa to C4H6+H = C2H4+C2H3

C6H7-135E3M+H = S1XC4H4-13E2M+C2H4 1.46E+30 -4.34 21647 ! Refa to C4H6+H = C2H4+C2H3

C6H7-135E3M+H = C4H5-13E2M+C2H3 1.46E+30 -4.34 21647 ! Refa to C4H6+H = C2H4+C2H3

C6H7-135E3M+H = C5H8-13E+C2H3 1.46E+30 -4.34 21647 ! Refa to C4H6+H = C2H4+C2H3

C6H7-135E3M+H = C6H8-135E+CH3 8.80E+16 -1.05 6461.0 ! Refa to C3H6+H = C2H4+CH3

C7H10-135E+H = T1XC5H7-13E+C2H4 1.46E+30 -4.34 21647 ! Refa to C4H6+H = C2H4+C2H3

C7H10-135E+H = C4H6+CH3CHCH 1.46E+30 -4.34 21647 ! Refa to C4H6+H = C2H4+C2H3

C7H10-135E+H = C6H8-135E+CH3 8.80E+16 -1.05 6461.0 ! Refa to C3H6+H = C2H4+CH3

C7H10-135E+H = C5H8-13E+C2H3 1.46E+30 -4.34 21647 ! Refa to C4H6+H = C2H4+C2H3

C7H10-135E+H = nC4H5+C3H6 1.46E+30 -4.34 21647 ! Refa

! cyclic C7H11 reactions

S3XMCH-1E(+M)=MCH-13E+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW/ 3.07E-37 15.37 -603.1/

TROE /-51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

S2XMCH-6E(+M)=MCH-15E+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1/

TROE/ -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

T1XMCH-2E(+M)=MCH-15E+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1/

TROE/ -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

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T1XMCH-2E(+M)=CH2cC6H8-2E+H(+M) 4.70E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M)
LOW / 4.60E-37 15.37 -603.1/
TROE/ -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
S2XMCH-3E(+M)=MCH-35E+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) *2/3
LOW/ 3.07E-37 15.37 -603.1/
TROE /-51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
S2XMCH-3E(+M)=MCH-13E+H(+M) 1.57E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) *1/3
LOW/ 1.54E-37 15.37 -603.1/
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
S2XMCH-3E=cC6H8-13E+CH3 4.24E+21 -3.89 22867 ! Refa to S2XMCH=cC6H10+CH3
PLOG / 0.039 4.24E+21 -3.89 22867 / !
PLOG / 0.197 2.58E+22 -3.86 24360 / !
PLOG / 1.000 2.27E+28 -5.30 29571 / !
PLOG / 10.000 4.14E+38 -7.84 39088 / !
PLOG / 100.000 1.94E+45 -9.36 47105 / !
PLOG / 1.0E+5 6.35E+13 0.20 33524 / !
S5XMCH-3E(+M)=MCH-35E+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) *2/3
LOW/ 3.07E-37 15.37 -603.1/
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
! chain C7H11 reactions
S3XC7H11-16E(+M) = C4H6+aC3H5(+M) 3.39E+11 0.66 32262.9 ! Refa to S3XC6H11-1E(+M) = C4H6+C2H5(+M)
LOW / 4.00E-42 18.05 -602.6 /
TROE / -18.50 246 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S3XC7H11-15E = C7H10-135E+H 1.27E+24 -4.75 23777 ! Refa to C4H7 = C4H6+H
PLOG / 0.033 1.27E+24 -4.75 23777/
PLOG / 0.066 1.38E+26 -5.221 25729/
PLOG / 0.132 1.75E+28 -5.709 27764/
PLOG / 0.197 3.16E+29 -6.003 28985/
PLOG / 0.263 2.69E+30 -6.222 29890/
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PLOG / 1.0 2.48E+53 -12.30 52000/
PLOG / 10 1.85E+48 -10.50 51770/
C4H6+CH3CHCH =S3XC7H11-15E 1.23E+35 -7.76 9930.0 ! Refa to C2H4+C2H3 = C4H7
PLOG / 0.039 6.15E+34 -7.76 9930.0 /
PLOG / 0.1 1.23E+35 -7.76 9930.0 /
PLOG / 1.0 7.93E+38 -8.47 14220.0/
PLOG / 10 2.99E+36 -7.40 15480.0/
S4XC7H11-15E = C7H10-135E+H 1.27E+24 -4.75 23777 ! Refa to C4H7 = C4H6+H
PLOG / 0.033 1.27E+24 -4.75 23777 /
PLOG / 0.066 1.38E+26 -5.221 25729 /
PLOG / 0.132 1.75E+28 -5.709 27764 /
PLOG / 0.197 3.16E+29 -6.003 28985 /
PLOG / 0.263 2.69E+30 -6.222 29890 /
PLOG / 1.0 2.48E+53 -12.30 52000 /
PLOG / 10 1.85E+48 -10.50 51770 /
C5H8-13E+C2H3 = S4XC7H11-15E 1.23E+35 -7.76 9930.0 ! Refa to C2H4+C2H3 = C4H7
PLOG / 0.039 6.15E+34 -7.76 9930.0 /
PLOG / 0.1 1.23E+35 -7.76 9930.0 /
PLOG / 1.0 7.93E+38 -8.47 14220.0/
PLOG / 10 2.99E+36 -7.40 15480.0/
S7XC7H11-15E(+M) = C4H6+aC3H5(+M) 3.39E+11 0.66 32262.9 ! Refa to S3XC6H11-1E(+M) = C4H6+C2H5(+M)
LOW / 4.00E-42 18.05 -602.6 /
TROE / -18.50 246 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
T3XC6H8-15E3M = C6H7-135E3M+H 1.27E+24 -4.75 23777 ! Refa to C4H7 = C4H6+H
PLOG / 0.033 1.27E+24 -4.75 23777 /
PLOG / 0.066 1.38E+26 -5.221 25729 /
PLOG / 0.132 1.75E+28 -5.709 27764 /
PLOG / 0.197 3.16E+29 -6.003 28985 /
PLOG / 0.263 2.69E+30 -6.222 29890 /
PLOG / 1.0 2.48E+53 -12.30 52000 /
PLOG / 10 1.85E+48 -10.50 51770 /
C4H5-13E2M+C2H3 = T3XC6H8-15E3M 1.23E+35 -7.76 9930.0 ! Refa to C2H4+C2H3 = C4H7
PLOG / 0.039 6.15E+34 -7.76 9930.0 /
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PLOG / 0.1 1.23E+35 -7.76 9930.0 /
PLOG / 1.0 7.93E+38 -8.47 14220.0/
PLOG / 10 2.99E+36 -7.40 15480.0/
S4XC6H8-15E3M (+M) = C6H8-135E+CH3 (+M) 3.39E+11 0.66 32262.9 ! Refa S3XC6H11-1E(+M) = C4H6+C2H5(+M)
LOW / 4.00E-42 18.05 -602.6 /
TROE / -18.50 246 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C5H8-13E+C2H3 = S4XC6H8-15E3M 1.23E+35 -7.76 9930.0 ! Refa to C2H4+C2H3 = C4H7
PLOG / 0.039 6.15E+34 -7.76 9930.0 /
PLOG / 0.1 1.23E+35 -7.76 9930.0 /
PLOG / 1.0 7.93E+38 -8.47 14220.0/
PLOG / 10 2.99E+36 -7.40 15480.0/
S4XC6H8-15E3M(+M) = C6H7-135E3M+H(+M) 1.57E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *1/3
LOW/ 1.54E-37 15.37 -603.1 /
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
P1XCH2-3C6H9-15E(+M) = C4H6+aC3H5(+M) 4.57E+12 0.13 24386.4 ! Refa to S5XC6H11-1E(+M) = C3H6+aC3H5(+M)
LOW / 2.50E-31 14.57 -578.8/
TROE / -13.17 268 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S3XC6H8-15E2M = C6H7-135E2M+H 1.27E+24 -4.75 23777 ! Refa to C4H7 = C4H6+H
PLOG / 0.033 1.27E+24 -4.75 23777 /
PLOG / 0.066 1.38E+26 -5.221 25729 /
PLOG / 0.132 1.75E+28 -5.709 27764 /
PLOG / 0.197 3.16E+29 -6.003 28985 /
PLOG / 0.263 2.69E+30 -6.222 29890 /
PLOG / 1.0 2.48E+53 -12.30 52000 /
PLOG / 10 1.85E+48 -10.50 51770 /
C4H5-13E2M+C2H3 = S3XC6H8-15E2M 1.23E+35 -7.76 9930.0 ! Refa to C2H4+C2H3 = C4H7
PLOG / 0.039 6.15E+34 -7.76 9930.0 /
PLOG / 0.1 1.23E+35 -7.76 9930.0 /
PLOG / 1.0 7.93E+38 -8.47 14220.0/
PLOG / 10 2.99E+36 -7.40 15480.0/
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S4XC6H8-15E2M = C6H7-135E2M+H 1.27E+24 -4.75 23777 ! Refa to C4H7 = C4H6+H
PLOG / 0.033 1.27E+24 -4.75 23777 /
PLOG / 0.066 1.38E+26 -5.221 25729 /
PLOG / 0.132 1.75E+28 -5.709 27764 /
PLOG / 0.197 3.16E+29 -6.003 28985 /
PLOG / 0.263 2.69E+30 -6.222 29890 /
PLOG / 1.0 2.48E+53 -12.30 52000 /
PLOG / 10 1.85E+48 -10.50 51770 /
C4H6+CH3CCH2 = S4XC6H8-15E2M 1.23E+35 -7.76 9930.0 ! Refa to C2H4+C2H3 = C4H7
PLOG / 0.039 6.15E+34 -7.76 9930.0 /
PLOG / 0.1 1.23E+35 -7.76 9930.0 /
PLOG / 1.0 7.93E+38 -8.47 14220.0/
PLOG / 10 2.99E+36 -7.40 15480.0/
P1XCH2C6H9-15E=aC3H4+C4H7 1.00E+12 0.0 51000 ! Refa to iC4H7=aC3H4+CH3
PLOG / 0.039 1.00E+12 0.0 51000/ ! EST /10
PLOG / 1.0 1.00E+13 0.0 51000/ ! 2009 Yasunaga et al.
! cC7H12 reactions
MCH-1E+H = S3XMCH-1E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571
MCH-1E+CH3= S3XMCH-1E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
S3XMCH-1E+H(+M)=MCH-1E(+M) 1.33E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/3
LOW/ 0.89E+60 -12.00 5967.8 /
TROE /0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S2XMCH-6E+H(+M)=MCH-1E(+M) 1.33E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/3
LOW/ 0.89E+60 -12.00 5967.8 /
TROE /0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
MCH-1E+H = S2XMCH-6E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571
MCH-1E+CH3= S2XMCH-6E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
CH2S2XcC6H9+H(+M)=MCH-1E(+M) 2.00E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M)
LOW /1.33E+60 -12.00 5967.8/
TROE /0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
MCH-1E+H = CH2S2XcC6H9+H2 1.73E5 2.5 2492 ! allylp LLNL-MI-407571
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MCH-1E+CH3= CH2S2XcC6H9+CH4 2.2098 3.5 5675 ! allylp LLNL-MI-407571

MCH-2E+H = S2XMCH-3E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571

MCH-2E+CH3= S2XMCH-3E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

S2XMCH-3E+H(+M)=MCH-2E(+M) 1.33E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/

LOW/ 0.89E+60 -12.00 5967.8 /

TROE /0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

MCH-2E+H = T1XMCH-2E+H2 2.65E6 2.2 0.0 ! allylt LLNL-MI-407571

MCH-2E+CH3= T1XMCH-2E+CH4 4.613 3.1 2330 ! allylt LLNL-MI-407571

T1XMCH-2E+H(+M)=MCH-2E(+M) 0.67E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *1/3

LOW / 0.44E+60 -12.00 5967.8/

TROE / 0.020 1096.6 1096.6 6859.5/

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S2XcC6H9-1E+CH3(+M)=MCH-2E(+M) 1.00E+14 -0.32 -262. ! Refa to aC3H5+CH3(+M)=C4H8-1(+M)

LOW / 3.51E+60 -12.97 6000./

TROE / 0.896 60000 1606 6118/

H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/

MCH-3E+H = S2XMCH-3E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571

MCH-3E+CH3= S2XMCH-3E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

S2XMCH-3E+H(+M)=MCH-3E(+M) 1.33E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/3

LOW / 0.89E+60 -12.00 5967.8 /

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

MCH-3E+H = S5XMCH-3E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571

MCH-3E+CH3= S5XMCH-3E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

S5XMCH-3E+H(+M)=MCH-3E(+M) 1.33E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/3

LOW / 0.89E+60 -12.00 5967.8 /

TROE/ 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

CH2cC6H10+H = CH2S2XcC6H9+H2 6.752E05 2.36 207 ! (ax4) allyls LLNL-MI-407571

CH2cC6H10+CH3= CH2S2XcC6H9+CH4 7.38 3.31 4002 ! (ax4) allyls LLNL-MI-407571

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CH2S2XcC6H9+H(+M)=CH2cC6H10(+M) 4.0E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2
LOW / 2.66E+60 -12.00 5967.8 /
TROE/ 0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
CH2S2XcC6H9=C2H3-2-PXC5H8 1.24E+22 -4.01 22066 ! Refa to S2XMCH=P6XC6H10-1E3M ! 20131221 added
PLOG / 0.039 1.24E+22 -4.01 22066 / !
PLOG / 0.197 4.17E+22 -3.93 23430 / !
PLOG / 1.000 1.01E+28 -5.23 28271 / !
PLOG / 10.000 2.14E+37 -7.54 37062 / !
PLOG / 100.000 1.11E+43 -8.81 44209 / !
PLOG / 1.0E+5 1.59E+13 0.22 31118 / !
CH2S2XcC6H9=CH2cC6H8-2E+H 1.82E+20 -3.68 23447 ! Refa to S2XMCH=MCH-2E+H ! 20131221 added
PLOG / 0.039 1.82E+20 -3.68 23447 / !
PLOG / 0.197 1.92E+21 -3.70 25053 / !
PLOG / 1.000 5.62E+27 -5.27 30610 / !
PLOG / 10.000 7.34E+38 -8.02 40816 / !
PLOG / 100.000 2.67E+46 -9.75 49698 / !
PLOG / 1.0E+5 2.01E+12 0.63 35196 / !
CH2cC6H10+H = CH2S3XcC6H9+H2 2.6E+06 2.4 4471 ! secondary LLNL-MI-407571 ! 20131221 added 1.3E06 *2
CH2cC6H10+CH3 = CH2S3XcC6H9+CH4 3.0E+00 3.46 5481 ! secondary LLNL-MI-407571 ! 20131221 added 1.51 *2
CH2S3XcC6H9=CH2-4-PXC6H9 1.21E+18 -2.84 19903 ! Refa to S3XMCH=P6XC6H10-1E4M ! 20131221 added
PLOG / 0.039 1.21E+18 -2.84 19903 / !
PLOG / 0.197 7.98E+21 -3.70 23365 / !
PLOG / 1.000 2.52E+28 -5.31 28978 / !
PLOG / 10.000 8.05E+37 -7.66 38033 / !
PLOG / 100.000 6.13E+42 -8.70 44718 / !
PLOG / 1.0E+5 1.68E+13 0.21 31241 / !
CH2S3XcC6H9=CH2cC6H8-2E+H 1.27E+24 -4.75 23777 ! Refa to C4H7=C4H6+H ! 20131221 added
PLOG / 0.033 1.27E+24 -4.75 23777 / !
PLOG / 0.066 1.38E+26 -5.221 25729 / !
PLOG / 0.132 1.75E+28 -5.709 27764 / !
PLOG / 0.197 3.16E+29 -6.003 28985 / !
PLOG / 0.263 2.69E+30 -6.222 29890 / !
```

PLOG / 1.0 2.48E+53 -12.30 52000 / !

PLOG / 10 1.85E+48 -10.50 51770 / !

CH2-4-PXC6H9=CH2-3-C6H8-14+H 1.27E+24 -4.75 23777 ! Refa to C4H7=C4H6+H ! 20131221 added

PLOG / 0.033 1.27E+24 -4.75 23777 / !

PLOG / 0.066 1.38E+26 -5.221 25729 / !

PLOG / 0.132 1.75E+28 -5.709 27764 / !

PLOG / 0.197 3.16E+29 -6.003 28985 / !

PLOG / 0.263 2.69E+30 -6.222 29890 / !

PLOG / 1.0 2.48E+53 -12.30 52000 / !

PLOG / 10 1.85E+48 -10.50 51770 / !

CH2-3-C6H8-14+H = P1XCH2C4H5-13E+C2H4 8.80E+16 -1.05 6461.0 ! Refa C3H6+H = C2H4+CH3 ! 20131221 added

CH2-3-C6H8-14+H = C4H6+aC3H5 8.80E+16 -1.05 6461.0 ! Refa C3H6+H = C2H4+CH3 ! 20131221 added

CH2cC6H10+H = CH2S4XcC6H9+H2 1.3E06 2.4 4471 ! secondary LLNL-MI-407571 ! 20131221 added

CH2cC6H10+CH3 = CH2S4XcC6H9+CH4 1.51 3.46 5481 ! secondary LLNL-MI-407571 ! 20131221 added

CH2S4XcC6H9=CH2-5-PXC6H9 1.26E+22 -3.85 22627 ! Refa to S4XMCH

PLOG / 0.039 1.26E+22 -3.85 22627 / !

PLOG / 0.197 3.57E+26 -4.89 26638 / !

PLOG / 1.000 2.59E+32 -6.32 32020 / !

PLOG / 10.000 2.07E+41 -8.51 40814 / !

PLOG / 100.000 5.79E+44 -9.15 46530 / !

PLOG / 1.0E+5 3.87E+13 0.20 31782 / !

CH2-5-PXC6H9=aC3H4+C4H7 7.010E+10 1.38 56000 ! Refa to iC4H7=aC3H4+CH3, hpl,2005ZHE/SUN9044-9053 J. Phys. Chem. A 109

MCH-1E=C4H5-13E2M+C2H4 5.0E+78 -18.94 98386 ! Refa to cC6H10 = C4H6+C2H4

PLOG / 0.039 5.0E+78 -18.94 98386 /

PLOG / 0.197 2.60E+70 -16.36 95510 /

PLOG / 1.0 3.81E+25 -3.58 64034 /

PLOG / 1.0E+5 8.31E+13 0.387 64116 /

MCH-2E=C5H8-13E+C2H4 5.0E+78 -18.94 98386 ! Refa to cC6H10 = C4H6+C2H4

PLOG / 0.039 5.0E+78 -18.94 98386 /

PLOG / 0.197 2.60E+70 -16.36 95510 /

PLOG / 1.0 3.81E+25 -3.58 64034 /

PLOG / 1.0E+5 8.31E+13 0.387 64116 /

MCH-3E=C4H6+C3H6 5.0E+78 -18.94 98386 ! Refa to cC6H10 = C4H6+C2H4

```
PLOG / 0.039 5.0E+78 -18.94 98386 /
PLOG / 0.197 2.60E+70 -16.36 95510 /
PLOG / 1.0 3.81E+25 -3.58 64034 /
PLOG / 1.0E+5 8.31E+13 0.387 64116 /
CH2cC6H10=C6H9-15E2M 1.33E+137 -34.70 162775 ! Refa to cC6H12
PLOG / 0.039 1.33E+137 -34.70 162775/ !
PLOG / 0.066 5.96E+139 -35.26 166598/ !
PLOG / 0.263 1.82E+143 -35.99 172904/ !
PLOG / 1.0E+5 8.76E+17 0.00 91940 / !
! C7H12 dienes reactions
C7H12-13E+H = C5H10-1E+C2H3 1.46E+30 -4.34 21647.0 ! =(C4H6+H)
C7H12-13E= C2H5+lC5H7 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7
PLOG / 0.039 1.07E+80 -19.33 95177/
PLOG / 0.066 2.50E+68 -16.040 86832/
PLOG / 0.132 1.480E+59 -13.261 82596/
PLOG / 0.197 2.43E+61 -13.999 82637/
PLOG / 0.263 3.75E+59 -13.427 82179/
PLOG / 1.0E+5 1.46E+16 0.00 69120/
C7H12-16E=aC3H5+C4H7 2.14E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7 *2
PLOG / 0.039 2.14E+80 -19.33 95177/
PLOG / 0.066 5.00E+68 -16.040 86832/
PLOG / 0.132 2.96E+59 -13.261 82596/
PLOG / 0.197 4.86E+61 -13.999 82637/
PLOG / 0.263 7.50E+59 -13.427 82179/
PLOG / 1.0E+5 2.92E+16 0.00 69120/
C7H12-16E+H = S3XC7H11-16E+H2 6.752E+5 2.36 207 ! (ax4) allyls LLNL-MI-407571
C7H12-16E+CH3 = S3XC7H11-16E+CH4 7.38 3.31 4002 ! (ax4) allyls LLNL-MI-407571
C7H12-15E= aC3H5+SAXC4H7 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7
PLOG / 0.039 1.07E+80 -19.33 95177/
PLOG / 0.066 2.50E+68 -16.040 86832/
PLOG / 0.132 1.480E+59 -13.261 82596/
PLOG / 0.197 2.43E+61 -13.999 82637/
PLOG / 0.263 3.75E+59 -13.427 82179/
PLOG / 1.0E+5 1.46E+16 0.00 69120/
C7H12-15E+H =S3XC7H11-15E+H2 3.376E5 2.36 207 ! allyls LLNL-MI-407571
```

C7H12-15E+H = S4XC7H11-15E+H2 3.376E5 2.36 207 ! allyls LLNL-MI-407571

C7H12-15E+CH3 =S3XC7H11-15E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C7H12-15E+CH3 = S4XC7H11-15E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C7H12-15E+H = S7XC7H11-15E+H2 1.7298E5 2.5 2492 ! allylP LLNL-MI-407571

C7H12-15E+CH3 = S7XC7H11-15E+CH4 2.2098 3.5 5675 ! allylP LLNL-MI-407571

C6H9-15E3M = aC3H5+SAXC4H7 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

C6H9-15E3M = S3XC6H9-15E+CH3 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

C6H9-15E3M+H = S4XC6H8-15E3M+H2 3.376E5 2.36 207 ! allyls LLNL-MI-407571

C6H9-15E3M+CH3 = S4XC6H8-15E3M+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C6H9-15E3M+H = P1XCH2-3C6H9-15E+H2 6.651E05 2.54 6756 ! primary LLNL-MI-407571

C6H9-15E3M+CH3 = P1XCH2-3C6H9-15E+CH4 4.521E-1 3.65 7154 ! primary LLNL-MI-407571

C6H9-15E3M+H = T3XC6H8-15E3M+H2 2.65E6 2.2 0.0 ! allylt LLNL-MI-407571

C6H9-15E3M+CH3 = T3XC6H8-15E3M+CH4 4.613 3.1 2330 ! allylt LLNL-MI-407571

C7H12-24E = S5XC6H9-13E+CH3 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

CH2-3-C6H10-1E = P1XCH2C4H5-13E+C2H5 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

CH2-3-C6H10-1E+H = C5H10-1E+C2H3 1.46E+30 -4.34 21647.0 ! =(C4H6+H)

CH2-3-C6H10-1E+H = C4H6+nC3H7 8.80E+16 -1.05 6461.0 ! Refa to C3H6+H = C2H4+CH3

CH2-3-C6H10-1E+H = C4H5-13E2M+C2H5 3.20E+22 -2.39 11180 ! Refa to C4H8-1+H = C3H6+CH3

C6H9-15E2M+H = S3XC6H8-15E2M+H2 3.376E5 2.36 207 ! allyls LLNL-MI-407571

C6H9-15E2M+H = S4XC6H8-15E2M+H2 3.376E5 2.36 207 ! allyls LLNL-MI-407571

C6H9-15E2M+H = P1XCH2C6H9-15E+H2 1.7298E5 2.5 2492 ! allylp LLNL-MI-407571

C6H9-15E2M+CH3 = S3XC6H8-15E2M+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C6H9-15E2M+CH3 = S4XC6H8-15E2M+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C6H9-15E2M+CH3 = P1XCH2C6H9-15E+CH4 2.2098 3.5 5675 ! allylp LLNL-MI-407571

C6H9-15E2M = aC3H5+iC4H7 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

C6H9-13E5M = S5XC6H9-13E+CH3 2.14E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7 *2

PLOG / 0.039 2.14E+80 -19.33 95177/

PLOG / 0.066 5.00E+68 -16.040 86832/

PLOG / 0.132 2.96E+59 -13.261 82596/

PLOG / 0.197 4.86E+61 -13.999 82637/

PLOG / 0.263 7.50E+59 -13.427 82179/

PLOG / 1.0E+5 2.92E+16 0.00 69120/

! C7H13 alkenyl reactions

P7XC7H13-1E (+M) = C2H4+P5XC5H9-1E (+M) 3.98E+12 0.12 27571.6 ! Refa to P6XC6H11-1E(+M) = C4H7+C2H4(+M)

LOW / 3.30E-43 18.35 -602.5/

TROE / -13.87 227 28 50000.0/

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C7H12-16E+H(+M) = P7XC7H13-1E(+M) 1.33E+13 0.00 3260.7 ! Refa to C3H6+H(+M) = nC3H7(+M)

LOW / 6.26E+38 -6.66 7000.0/

TROE / 1.000 1000.0 1310.0 48097.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

P7XC7H13-1E(+M) = S3XC7H13-1E(+M) 1.55E+02 2.83 15566.2 ! Refa to PXC6H11(+M) = S3XC6H11-1E(+M)

LOW / 1.50E-30 14.56 -602.4/

TROE / -13.59 214 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S6XC7H13-1E(+M) = C4H7+C3H6(+M) 5.50E+11 0.55 28084.3 ! 08TSAb JetSurF 2.0

LOW/ 3.10E-43 18.418 -602.9 /

TROE/ -32.13 207.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S6XC7H13-1E(+M) = S3XC7H13-1E(+M) 1.55E+02 2.83 15566.2 ! 08/TSwip JetSurF 2.0

LOW/ 1.50E-30 14.56 -602.4 /

TROE/ -13.59 214 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C7H12-16E+H(+M) = S6XC7H13-1E(+M) 1.33E+13 0.00 1559.8 ! Refa to C4H8-1+H(+M) = sC4H9(+M)

LOW / 8.70E+42 -7.50 4721.8/

TROE / 1.000 1000.0 645.4 6844.3 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C7H12-15E+H(+M) = S6XC7H13-1E(+M) 1.33E+13 0.00 1559.8 ! Refa to C4H8-2+H(+M) = sC4H9(+M)

LOW / 8.70E+42 -7.50 4721.8 /

TROE / 1.000 1000.0 645.4 6844.3 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S3XC7H13-1E(+M) = C4H6+nC3H7(+M) 3.39E+11 0.66 32262.9 ! 08/TSAwip JetSurF 2.0

LOW/ 4.00E-42 18.045 -602.6 /

TROE/ -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S3XC7H13-1E(+M) = C7H12-13E+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7 = C4H6 + H *2/3

LOW / 3.07E-37 15.37 -603.1/

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

P6XC6H10-1E4M(+M) = S4XC5H9-1E+C2H4(+M) 1.76E+11 0.57 28791.0 ! 08TSAa JetSurF 2.0

LOW/ 2.80E-44 18.729 -602.5 /

TROE / -14.66 219.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C6H9-15E3M+H(+M) = P6XC6H10-1E4M(+M) 1.33E+13 0.00 3260.7 ! Refa to C3H6+H(+M) = nC3H7(+M)

LOW / 6.26E+38 -6.66 7000.0/

TROE / 1.000 1000.0 1310.0 48097.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

P6XC6H10-1E4M(+M) = S3XC6H10-1E4M(+M) 1.55E+02 2.83 15566.2 ! 08/TSwip JetSurF 2.0

LOW/ 1.50E-30 14.56 -602.4 /

TROE/ -13.59 214 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S3XC6H10-1E4M(+M) = C5H8-13E+C2H5(+M) 3.39E+11 0.66 31262.9 ! 08/TSAwip (-1 kcal/mol Ctert-Csec) JetSurF 2.0

LOW / 4.00E-42 18.045 -602.6/

TROE / -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S3XC6H10-1E4M(+M) = C6H10-13E+CH3(+M) 3.39E+11 0.66 31262.9 ! Refa to S3XC6H11-1E(+M) = C4H6+C2H5(+M)

LOW / 4.00E-42 18.045 -602.6/

TROE / -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

P7XC7H13-2E(+M) = S3XC5H9-1E+C2H4(+M) 9.12E+11 0.31 27237.8 ! 08TSAb (lumped C5H9) JetSurF 2.0

LOW / 1.80E-57 23.463 -602.4 /

TROE/ -2.46 206.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C7H12-15E+H(+M) = P7XC7H13-2E(+M) 1.33E+13 0.00 3260.7 ! Refa to C3H6+H(+M) = nC3H7(+M)

LOW / 6.26E+38 -6.66 7000.0/

TROE / 1.000 1000.0 1310.0 48097.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

P7XC7H13-2E(+M) = S4XC7H13-2E(+M) 1.55E+02 2.83 15566.2 ! 08/TSwip JetSurF 2.0

LOW / 1.50E-30 14.56 -602.4 /

TROE / -13.59 214 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S4XC7H13-2E(+M) = C5H8-13E+C2H5(+M) 3.39E+11 0.66 32262.9 ! Refa to S3XC6H11-1E(+M) = C4H6+C2H5(+M)

LOW / 4.00E-42 18.05 -602.6 /

TROE/ -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S4XC7H13-2E(+M) = C7H12-24E+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7 = C4H6 + H *2/3

LOW / 3.07E-37 15.37 -603.1/

TROE/ -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

S4XC7H13-2E(+M) = C7H12-13E+H(+M) 4.70E+08 1.32 44697.6 ! Refa to SAXC4H7 = C4H6 + H

LOW / 4.60E-37 15.37 -603.1/

TROE/ -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

P6XC6H10-1E3M(+M) = P4XC4H6-1E3M+C2H4(+M) 2.38E+11 0.51 27281.5 ! 08TSAb JetSurF 2.0

LOW / 1.80E-57 23.463 -602.4 /

TROE / -2.46 206.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C6H9-15E3M+H(+M) = P6XC6H10-1E3M(+M) 1.33E+13 0.00 3260.7 ! Refa to C3H6+H(+M) = nC3H7(+M)

LOW / 6.26E+38 -6.66 7000.0/

TROE / 1.000 1000.0 1310.0 48097.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

```
P6XC6H10-1E3M(+M) = T3XC6H10-1E3M(+M) 8.60E+01 2.62 8722.9 ! 08TSAc & Est-2 JetSurF 2.0
LOW / 8.10E-33 15.214 -677.4/
TROE / -30.39 206.0 28.0 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
T3XC6H10-1E3M(+M) = C4H5-13E2M+C2H5(+M) 3.39E+11 0.66 32262.9 ! Refa to S3XC6H11-1E(+M) = C4H6+C2H5(+M)
LOW / 4.00E-42 18.05 -602.6 /
TROE /-18.50 246 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
P6XC6H10-1E5M(+M) = C4H7+C3H6(+M) 1.76E+11 0.57 28791.6 ! 08TSAc (2-methyl-pent-4-yl) JetSurF 2.0
LOW / 4.70E-39 16.77 -603.1/
TROE /-27.89 216 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
P6XC6H10-1E5M(+M) = C6H10-15E+CH3(+M) 1.76E+11 0.57 28791.6 ! 08TSAc (2-methyl-pent-4-yl) JetSurF 2.0
LOW / 4.70E-39 16.77 -603.1/
TROE/ -27.89 216 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C6H9-15E2M+H(+M) = P6XC6H10-1E5M(+M) 1.33E+13 0.00 3260.7 ! Refa to iC4H8+H(+M) = iC4H9(+M)
LOW / 6.26E+38 -6.66 7000.0 /
TROE / 1.000 1000 1310.0 48097.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
P6XC6H10-1E5M(+M) = S3XC6H10-1E5M(+M) 1.55E+02 2.83 15566.2 ! 08/TSwip JetSurF 2.0
LOW / 1.50E-30 14.56 -602.4 /
TROE/ -13.59 214 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S3XC6H10-1E5M(+M) = C4H6+iC3H7(+M) 3.39E+11 0.66 31262.9 ! 08/TSAwip (-1 kcal/mol Ctert-Csec) JetSurF 2.0
LOW / 4.00E-42 18.045 -602.6/
TROE /-18.50 246 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S3XC6H10-1E5M(+M) = C6H9-13E5M+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7 = C4H6 + H *2/3
LOW / 3.07E-37 15.37 -603.1/
TROE /-51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
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P6XC6H10-1E2M(+M) = P4XC4H6-1E2M+C2H4(+M) 3.98E+12 0.12 27571.6 ! 08/TSAwip JetSurF 2.0
LOW / 3.30E-43 18.35 -602.5 /
TROE /-13.87 227 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C6H9-15E2M+H(+M) = P6XC6H10-1E2M(+M) 1.33E+13 0.00 3260.7 ! Refa to C3H6+H(+M) = nC3H7(+M)
LOW / 6.26E+38 -6.66 7000.0/
TROE / 1.000 1000.0 1310.0 48097.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
P6XC6H10-1E2M(+M) = S3XC6H10-1E2M(+M) 1.55E+02 2.83 15566.2 ! 08/TSwip JetSurF 2.0
LOW / 1.50E-30 14.56 -602.4 /
TROE /-13.59 214 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S3XC6H10-1E2M(+M) = C4H5-13E2M+C2H5(+M) 3.39E+11 0.66 32262.9 ! Refa to S3XC6H11-1E(+M) = C4H6+C2H5(+M)
LOW / 4.00E-42 18.05 -602.6 /
TROE / -18.50 246 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
! methylcyclohexyl (C7H13) reactions
PXCH2cC6H11 = S3XMCH 2.30E+07 1.02 28687.0 !
PLOG / 0.039 2.30E+07 1.02 28687.0/ ! 4.65E+08 /20 EST
PLOG / 1.000 4.65E+08 1.02 28687.0/ ! 09/SI-WA JetSurF 2.0
PXCH2cC6H11 = S4XMCH 6.0E+07 0.92 22700.0 !
PLOG / 0.039 6.0E+07 0.92 22700.0/ ! 1.19E+09 /20 EST
PLOG / 1.000 1.19E+09 0.92 22700.0/ ! 09/SI-W JetSurF 2.0
PXCH2cC6H11=P7XC7H13-1E 8.92E+18 -2.94 19897 ! calculated in this work
PLOG / 0.039 8.92E+18 -2.94 19897 / ! 800 K-2000 K
PLOG / 0.197 6.83E+22 -3.82 23511 / ! 800 K-2000 K
PLOG / 1.000 1.56E+29 -5.39 29211 / ! 800 K-2000 K
PLOG / 10.000 4.15E+37 -7.44 37753 / ! 800 K-2000 K
PLOG / 100.000 1.92E+39 -7.58 42286 / ! 800 K-2000 K
PLOG / 1.0E+5 2.53E+13 0.16 29785 / ! 800 K-2000 K
PXCH2cC6H11=CH2cC6H10+H 8.14E+14 -2.42 21719 ! calculated in this work
PLOG / 0.039 8.14E+14 -2.42 21719 / ! 800 K-2000 K
PLOG / 0.197 1.23E+20 -3.61 26095 / ! 800 K-2000 K
PLOG / 1.000 1.18E+28 -5.58 32946 / ! 800 K-2000 K
PLOG / 10.000 1.31E+39 -8.28 43693 / ! 800 K-2000 K
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PLOG / 100.000 4.67E+42 -8.87 50298 / ! 800 K-2000 K
PLOG / 1.0E+5 1.60E+11 0.59 35447 / ! 800 K-2000 K
T1XMCH=P6XC6H10-1E2M 7.77E+21 -3.78 22330 ! calculated in this work
PLOG / 0.039 7.77E+21 -3.78 22330 / ! 800 K-2000 K
PLOG / 0.197 2.46E+23 -3.98 24528 / ! 800 K-2000 K
PLOG / 1.000 3.46E+31 -6.06 31348 / ! 800 K-2000 K
PLOG / 10.000 3.04E+40 -8.25 40204 / ! 800 K-2000 K
PLOG / 100.000 3.40E+43 -8.78 45692 / ! 800 K-2000 K
PLOG / 1.0E+5 2.51E+13 0.24 31344 / ! 800 K-2000 K
T1XMCH=CH2cC6H10+H 5.68E+24 -4.98 28465 ! calculated in this work
PLOG / 0.039 5.68E+24 -4.98 28465 / ! 800 K-2000 K
PLOG / 0.197 4.63E+25 -4.97 30017 / ! 800 K-2000 K
PLOG / 1.000 2.67E+34 -7.20 37107 / ! 800 K-2000 K
PLOG / 10.000 4.39E+44 -9.70 46944 / ! 800 K-2000 K
PLOG / 100.000 1.12E+49 -10.55 53815 / ! 800 K-2000 K
PLOG / 1.0E+5 1.18E+14 -0.04 37343 / ! 800 K-2000 K
T1XMCH=MCH-1E+H 1.47E+22 -4.09 24874 ! calculated in this work
PLOG / 0.039 1.47E+22 -4.09 24874 / ! 800 K-2000 K
PLOG / 0.197 1.57E+23 -4.12 26671 / ! 800 K-2000 K
PLOG / 1.000 7.83E+31 -6.33 33844 / ! 800 K-2000 K
PLOG / 10.000 6.83E+41 -8.76 43572 / ! 800 K-2000 K
PLOG / 100.000 7.93E+45 -9.52 50174 / ! 800 K-2000 K
PLOG / 1.0E+5 5.80E+12 0.46 34881 / ! 800 K-2000 K
S2XMCH=P6XC6H10-1E3M 1.24E+22 -4.01 22066 ! calculated in this work
PLOG / 0.039 1.24E+22 -4.01 22066 / ! 800 K-2000 K
PLOG / 0.197 4.17E+22 -3.93 23430 / ! 800 K-2000 K
PLOG / 1.000 1.01E+28 -5.23 28271 / ! 800 K-2000 K
PLOG / 10.000 2.14E+37 -7.54 37062 / ! 800 K-2000 K
PLOG / 100.000 1.11E+43 -8.81 44209 / ! 800 K-2000 K
PLOG / 1.0E+5 1.59E+13 0.22 31118 / ! 800 K-2000 K
S2XMCH=P7XC7H13-2E 2.99E+22 -4.04 21843 ! calculated in this work
PLOG / 0.039 2.99E+22 -4.04 21843 / ! 800 K-2000 K
PLOG / 0.197 8.66E+22 -3.95 23164 / ! 800 K-2000 K
PLOG / 1.000 1.44E+28 -5.21 27888 / ! 800 K-2000 K
PLOG / 10.000 1.61E+37 -7.45 36452 / ! 800 K-2000 K
PLOG / 100.000 4.39E+42 -8.66 43334 / ! 800 K-2000 K
PLOG / 1.0E+5 2.37E+13 0.19 30429 / ! 800 K-2000 K
S2XMCH=MCH-1E+H 2.06E+20 -3.80 23117 ! calculated in this work
PLOG / 0.039 2.06E+20 -3.80 23117 / ! 800 K-2000 K
PLOG / 0.197 1.50E+21 -3.78 24651 / ! 800 K-2000 K
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PLOG / 1.000 2.14E+27 -5.27 30013 / ! 800 K-2000 K
PLOG / 10.000 8.88E+37 -7.90 39841 / ! 800 K-2000 K
PLOG / 100.000 9.49E+44 -9.50 48246 / ! 800 K-2000 K
PLOG / 1.0E+5 5.69E+11 0.60 34004 / ! 800 K-2000 K
S2XMCH=MCH-2E+H 1.82E+20 -3.68 23447 ! calculated in this work
PLOG / 0.039 1.82E+20 -3.68 23447 / ! 800 K-2000 K
PLOG / 0.197 1.92E+21 -3.70 25053 / ! 800 K-2000 K
PLOG / 1.000 5.62E+27 -5.27 30610 / ! 800 K-2000 K
PLOG / 10.000 7.34E+38 -8.02 40816 / ! 800 K-2000 K
PLOG / 100.000 2.67E+46 -9.75 49698 / ! 800 K-2000 K
PLOG / 1.0E+5 2.01E+12 0.63 35196 / ! 800 K-2000 K
S2XMCH=cC6H10+CH3 4.24E+21 -3.89 22867 ! calculated in this work
PLOG / 0.039 4.24E+21 -3.89 22867 / ! 800 K-2000 K
PLOG / 0.197 2.58E+22 -3.86 24360 / ! 800 K-2000 K
PLOG / 1.000 2.27E+28 -5.30 29571 / ! 800 K-2000 K
PLOG / 10.000 4.14E+38 -7.84 39088 / ! 800 K-2000 K
PLOG / 100.000 1.94E+45 -9.36 47105 / ! 800 K-2000 K
PLOG / 1.0E+5 6.35E+13 0.20 33524 / ! 800 K-2000 K
S3XMCH=P6XC6H10-1E4M 1.21E+18 -2.84 19903 ! calculated in this work
PLOG / 0.039 1.21E+18 -2.84 19903 / ! 800 K-2000 K
PLOG / 0.197 7.98E+21 -3.70 23365 / ! 800 K-2000 K
PLOG / 1.000 2.52E+28 -5.31 28978 / ! 800 K-2000 K
PLOG / 10.000 8.05E+37 -7.66 38033 / ! 800 K-2000 K
PLOG / 100.000 6.13E+42 -8.70 44718 / ! 800 K-2000 K
PLOG / 1.0E+5 1.68E+13 0.21 31241 / ! 800 K-2000 K
S3XMCH=S6XC7H13-1E 5.23E+18 -2.93 19555 ! calculated in this work
PLOG / 0.039 5.23E+18 -2.93 19555 / ! 800 K-2000 K
PLOG / 0.197 2.06E+22 -3.73 22876 / ! 800 K-2000 K
PLOG / 1.000 3.29E+28 -5.27 28275 / ! 800 K-2000 K
PLOG / 10.000 3.31E+37 -7.49 36918 / ! 800 K-2000 K
PLOG / 100.000 8.80E+41 -8.42 43157 / ! 800 K-2000 K
PLOG / 1.0E+5 2.55E+13 0.17 30061 / ! 800 K-2000 K
S3XMCH=MCH-3E+H 1.19E+16 -2.44 20998 ! calculated in this work
PLOG / 0.039 1.19E+16 -2.44 20998 / ! 800 K-2000 K
PLOG / 0.197 5.50E+20 -3.50 24928 / ! 800 K-2000 K
PLOG / 1.000 1.93E+28 -5.37 31247 / ! 800 K-2000 K
PLOG / 10.000 3.19E+39 -8.14 41683 / ! 800 K-2000 K
PLOG / 100.000 1.03E+46 -9.58 49952 / ! 800 K-2000 K
PLOG / 1.0E+5 1.87E+12 0.63 34980 / ! 800 K-2000 K
S3XMCH=MCH-2E+H 6.78E+14 -2.23 21396 ! calculated in this work
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PLOG / 0.039 6.78E+14 -2.23 21396 / ! 800 K-2000 K
PLOG / 0.197 8.10E+19 -3.39 25518 / ! 800 K-2000 K
PLOG / 1.000 8.05E+27 -5.38 32106 / ! 800 K-2000 K
PLOG / 10.000 6.73E+39 -8.33 43061 / ! 800 K-2000 K
PLOG / 100.000 1.12E+47 -9.95 51964 / ! 800 K-2000 K
PLOG / 1.0E+5 1.64E+12 0.61 36658 / ! 800 K-2000 K
S4XMCH=P6XC6H10-1E5M 1.26E+22 -3.85 22627 ! calculated in this work
PLOG / 0.039 1.26E+22 -3.85 22627 / ! 800 K-2000 K
PLOG / 0.197 3.57E+26 -4.89 26638 / ! 800 K-2000 K
PLOG / 1.000 2.59E+32 -6.32 32020 / ! 800 K-2000 K
PLOG / 10.000 2.07E+41 -8.51 40814 / ! 800 K-2000 K
PLOG / 100.000 5.79E+44 -9.15 46530 / ! 800 K-2000 K
PLOG / 1.0E+5 3.87E+13 0.20 31782 / ! 800 K-2000 K
S4XMCH=MCH-3E+H 8.38E+20 -3.63 23771 ! calculated in this work
PLOG / 0.039 8.38E+20 -3.63 23771 / ! 800 K-2000 K
PLOG / 0.197 8.32E+25 -4.80 28120 / ! 800 K-2000 K
PLOG / 1.000 5.73E+32 -6.47 34206 / ! 800 K-2000 K
PLOG / 10.000 1.37E+43 -9.02 44242 / ! 800 K-2000 K
PLOG / 100.000 7.21E+47 -9.98 51272 / ! 800 K-2000 K
PLOG / 1.0E+5 3.78E+12 0.63 34881 / ! 800 K-2000 K
! methylcyclohexane reactions
! H-abstractions of methylcyclohexane
MCH+H = PXCH2cC6H11+H2 6.66E+06 2.13 8894.8 ! calculated in this work
MCH+H = T1XMCH+H2 4.53E+06 2.11 4098.6 ! calculated in this work
MCH+H = S2XMCH+H2 2.08E+07 2.10 6474.4 ! calculated in this work
MCH+H = S3XMCH+H2 2.07E+07 2.12 6441.2 ! calculated in this work
MCH+H = S4XMCH+H2 1.16E+07 2.11 6339.1 ! calculated in this work
MCH+CH3 = PXCH2cC6H11+CH4 3.75E+01 3.27 13516.0 ! 10LV JetSurF 2.0
MCH+CH3 = T1XMCH+CH4 1.91E+01 3.27 9022.0 ! 10LV JetSurF 2.0
MCH+CH3 = S2XMCH+CH4 6.68E+01 3.21 11418.0 ! 10LV JetSurF 2.0
MCH+CH3 = S3XMCH+CH4 7.18E+01 3.26 11303.0 ! 10LV JetSurF 2.0
MCH+CH3 = S4XMCH+CH4 1.82E+01 3.36 10931.0 ! 10LV JetSurF 2.0
! isomerization and decomposition of methylcyclohexane
MCH = cC6H11+CH3 1.00 0.00 0.00 ! 2013 Zhang et al.
PLOG / 0.01 1.85E+105 -26.15 129214 /
PLOG / 0.0395 1.19E+92 -22.23 122595 /
PLOG / 0.197 1.50E+80 -18.67 116938 /
PLOG / 0.395 8.65E+63 -13.89 108211 /
PLOG / 1 5.93E+64 -14.15 108486 /
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PLOG / 10 3.59E+45 -8.56 97430 /
PLOG / 100 1.66E+33 -4.99 90100 /
PLOG / 1.0E+5 1.10E+27 -3.20 86385 /
MCH = C7H14-1E 1.00 0.00 0.00 ! 2013 Zhang et al.
PLOG / 0.01 5.49E+115 -29.26 143180 /
PLOG / 0.0395 1.03E+104 -25.68 138280 /
PLOG / 0.197 1.92E+88 -20.96 130954 /
PLOG / 0.395 3.07E+80 -18.65 126930 /
PLOG / 1 5.57E+69 -15.49 121178 /
PLOG / 10 4.90E+44 -8.17 107073 /
PLOG / 100 7.98E+26 -3.02 96627 /
PLOG / 1.0E+5 1.09E+17 -0.16 90732 /
MCH = C7H14-2E 1.00 0.00 0.00 ! 2013 Zhang et al.
PLOG / 0.01 9.52E+114 -28.98 140737 /
PLOG / 0.0395 1.74E+103 -25.40 135829 /
PLOG / 0.197 3.34E+87 -20.68 128511 /
PLOG / 0.395 5.32E+79 -18.37 124487 /
PLOG / 1 9.66E+68 -15.21 118735 /
PLOG / 10 8.51E+43 -7.89 104630 /
PLOG / 100 1.38E+26 -2.74 94184 /
PLOG / 1.0E+5 1.90E+16 0.12 88289 /
MCH = C6H11-1E2M 1.00 0.00 0.00 ! 2013 Zhang et al.
PLOG / 0.01 2.25E+132 -34.10 155250 /
PLOG / 0.0395 1.46E+109 -27.20 144350 /
PLOG / 0.197 4.09E+93 -22.49 137505 /
PLOG / 0.395 4.87E+85 -20.13 133555 /
PLOG / 1 3.27E+74 -16.83 127710 /
PLOG / 10 3.09E+47 -8.92 112705 /
PLOG / 100 2.18E+27 -3.08 100948 /
PLOG / 1.0E+5 6.04E+15 0.27 94051 /
MCH = C6H11-1E5M 1.00 0.00 0.00 ! 2013 Zhang et al.
PLOG / 0.01 1.99E+132 -34.11 154207 /
PLOG / 0.0395 1.28E+109 -27.20 143306 /
PLOG / 0.197 3.61E+93 -22.49 136462 /
PLOG / 0.395 4.30E+85 -20.13 132511 /
PLOG / 1 2.89E+74 -16.83 126667 /
PLOG / 10 2.73E+47 -8.93 111662 /
PLOG / 100 1.93E+27 -3.08 99905 /
PLOG / 1.0E+5 5.34E+15 0.27 93008 /
MCH = C6H11-1E3M 1.00 0.00 0.00 ! 2013 Zhang et al.
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PLOG / 0.01 1.70E+119 -30.34 147025 /
PLOG / 0.0395 1.77E+108 -26.94 142902 /
PLOG / 0.197 4.67E+92 -22.23 136004 /
PLOG / 0.395 4.07E+107 -26.52 143245 /
PLOG / 1 3.71E+73 -16.58 126164 /
PLOG / 10 5.09E+46 -8.72 111220 /
PLOG / 100 6.68E+26 -2.95 99619 /
PLOG / 1.0E+5 2.53E+15 0.36 92802 /
MCH = C6H11-1E4M 1.00 0.00 0.00 ! 2013 Zhang et al.
PLOG / 0.01 1.87E+119 -30.34 146825 /
PLOG / 0.0395 1.95E+108 -26.95 142703 /
PLOG / 0.197 5.13E+92 -22.24 135803 /
PLOG / 0.395 4.47E+107 -26.52 143045 /
PLOG / 1 4.07E+73 -16.58 125964 /
PLOG / 10 5.59E+46 -8.72 111019 /
PLOG / 100 7.33E+26 -2.95 99418 /
PLOG / 1.0E+5 2.78E+15 0.35 92602 /
!C7H14 alkenes reactions
C7H14-1E = pC4H9+aC3H5 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7
PLOG / 0.039 1.07E+80 -19.33 95177/
PLOG / 0.066 2.50E+68 -16.040 86832/
PLOG / 0.132 1.480E+59 -13.261 82596/
PLOG / 0.197 2.43E+61 -13.999 82637/
PLOG / 0.263 3.75E+59 -13.427 82179/
PLOG / 1.0E+5 1.46E+16 0.00 69120/
C7H14-1E = C4H8-1+C3H6 7.08E+06 1.65 53752.0 !
PLOG / 0.039 3.54E+05 1.65 53752.0/ ! /20 EST
PLOG / 1.0 7.08E+06 1.65 53752.0/ ! JetSurF 2.0
C7H14-1E+H = S3XC7H13-1E+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571
C7H14-1E+CH3 = S3XC7H13-1E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
C7H14-2E = SAXC4H7+nC3H7 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7
PLOG / 0.039 1.07E+80 -19.33 95177 /
PLOG / 0.066 2.50E+68 -16.040 86832 /
PLOG / 0.132 1.480E+59 -13.261 82596 /
PLOG / 0.197 2.43E+61 -13.999 82637 /
PLOG / 0.263 3.75E+59 -13.427 82179 /
PLOG / 1.0E+5 1.46E+16 0.00 69120 /
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C7H14-2E = C4H8-1+C3H6 1.42E+07 1.65 53752.0 !

PLOG / 0.039 7.0E+05 1.65 53752.0/ ! /20 EST

PLOG / 1.0 1.42E+07 1.65 53752.0/ ! JetSurF 2.0

C7H14-2E+H = S3XC7H13-1E+H2 1.73E5 2.5 2492 ! allylp LLNL-MI-407571

C7H14-2E+CH3 = S3XC7H13-1E+CH4 2.2098 3.5 5675 ! allylp LLNL-MI-407571

C7H14-2E+H = S4XC7H13-2E+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C7H14-2E+CH3 = S4XC7H13-2E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C6H11-1E2M = iC4H7+nC3H7 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

C6H11-1E2M = iC4H8+C3H6 7.08E+06 1.65 53752.0 ! EST, refa to C7H14-1E

PLOG / 0.039 3.54E+05 1.65 53752.0/ !

PLOG / 1.0 7.08E+06 1.65 53752.0/ !

C6H11-1E2M+H = S3XC6H10-1E2M+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C6H11-1E2M+CH3 = S3XC6H10-1E2M+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C6H11-1E5M = aC3H5+iC4H9 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

C6H11-1E5M+H = S3XC6H10-1E5M+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C6H11-1E5M+CH3 = S3XC6H10-1E5M+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C6H11-1E4M = aC3H5+sC4H9 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

C6H11-1E4M = C3H6+C4H8-2 7.08E+06 1.65 53752.0 ! EST, refa to C7H14-1E

PLOG / 0.039 3.54E+05 1.65 53752.0/ !

PLOG / 1.0 7.08E+06 1.65 53752.0/ !

C6H11-1E4M+H = S3XC6H10-1E4M+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C6H11-1E4M+CH3 = S3XC6H10-1E4M+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C6H11-1E3M = SAXC4H7+nC3H7 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

C6H11-1E3M = S3XC6H11-1E+CH3 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

C6H11-1E3M = C4H8-2+C3H6 7.08E+06 1.65 53752.0 ! EST, refa to C7H14-1E

PLOG / 0.039 3.54E+05 1.65 53752.0/ !

PLOG / 1.0 7.08E+06 1.65 53752.0/ !

C6H11-1E3M+H = T3XC6H10-1E3M+H2 2.65E+6 2.2 0.0 ! allylt LLNL-MI-407571

C6H11-1E3M+CH3 = T3XC6H10-1E3M+CH4 4.613 3.1 2330 ! allylt LLNL-MI-407571

!!! ECH mechanism

! reactions of PAXCH2-2-1C4H7 (C5H9)

! PAXCH2-2-1C4H7 comes from C2H5-2-1C6H11

```
PAXCH2-2-1C4H7 = aC3H4+C2H5 2.00E+13 0.00 50078.0 !
PLOG / 0.039 1.00E+12 0.00 50078.0/ ! /20 EST
PLOG / 1.0E+5 2.00E+13 0.00 50078.0/ ! 73/TSA JetSurF 2.0
! reactions of P1XC4H82M (C5H11)
! P1XC4H82M come from C7H13-1E5M
CH3+C4H8-1(+M) = P1XC4H82M(+M) 4.80E+10 0.00 8003.6 ! Refa to C3H6+CH3(+M) = iC4H9(+M) /2
LOW / 6.50E+27 -4.27 2431.1 /
TROE / 0.565 60000.0 534.2 3007.2 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C2H5+C3H6(+M) = P1XC4H82M(+M) 4.80E+10 0.00 8003.6 ! Refa to C3H6+CH3(+M) = iC4H9(+M) /2
LOW / 6.50E+27 -4.27 2431.1 /
TROE / 0.565 60000.0 534.2 3007.2 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
! reactions of C2H3-2-PXC4H6, C2H3-3-PXC4H6
C2H4+iC4H5 = C2H3-2-PXC4H6 1.23E+35 -7.76 9930.0 ! Refa to C2H4+C2H3 = C4H7
PLOG / 0.039 6.15E+34 -7.76 9930.0 /
PLOG / 0.1 1.23E+35 -7.76 9930.0 /
PLOG / 1.0 7.93E+38 -8.47 14220.0/
PLOG / 10 2.99E+36 -7.40 15480.0/
C2H3+C4H6 = C2H3-3-PXC4H6 1.23E+35 -7.76 9930.0 ! Refa to C2H4+C2H3 = C4H7
PLOG / 0.039 6.15E+34 -7.76 9930.0 /
PLOG / 0.1 1.23E+35 -7.76 9930.0 /
PLOG / 1.0 7.93E+38 -8.47 14220.0/
PLOG / 10 2.99E+36 -7.40 15480.0/
! reactions of C6H11, P6XC6H11-2E, P5XC5H8-1E3M, P6XC6H11-3E, S4XC6H11-2E, PXCH2-3-1C5H9
! P6XC6H11-2E Come from P8XC8H15-2E
P6XC6H11-2E(+M) = SAXC4H7+C2H4(+M) 1.04E+12 -0.37 25124.2 ! 08/TSAwip
LOW / 5.90E-31 13.982 -603.1 /
TROE / -14.78 229 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
CH3S2XcC5H8=P6XC6H11-2E 4.27E+12 0.404 33710 ! HPL, 2-methylcyclopentyl radical decomposition, 2008 Sirjean et al. J. Phys. Chem. A 112 (2008) 11598-11610
CH3S2XcC5H8=P5XC5H8-1E3M 3.47E+10 0.959 33910 ! HPL, 2-methylcyclopentyl
```

radical decomposition, 2008 Sirjean et al. J. Phys. Chem. A 112 (2008) 11598-11610

! CH3S2XcC5H8=cC5H8+CH3 4.57E+11 0.843 30530 ! HPL, 2-methylcyclopentyl radical decomposition, 2008 Sirjean et al. J. Phys. Chem. A 112 (2008) 11598-11610

! P5XC5H8-1E3M Come from CH3S2XcC5H8 and P7XC7H12-1E3M

P5XC5H8-1E3M(+M) = SAXC4H7+C2H4(+M) 1.04E+12 -0.37 25124.2 ! Refa to P6XC6H11-2E

LOW / 5.90E-31 13.982 -603.1 /

TROE / -14.78 229 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

! P6XC6H11-3E Come from P8XC8H15-3E

P6XC6H11-3E(+M) = C6H10-13E+H(+M) 4.27E+09 -0.96 31962.9 ! 08/TSwip

LOW / 3.00E-45 13.55 -603.1 /

TROE/ -35.89 249 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

P6XC6H11-3E(+M) = S4XC6H11-2E(+M) 2.29E+01 2.82 10755.6 ! Refa to PXC8H17(+M) = S3XC8H17(+M), 1,5-H shift, in JetSurF 2.0, without considering the double bond

LOW / 9.90E-38 17.215 -603.0 /

TROE / -16.33 200.0 28.0 5000000 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S4XC6H11-2E(+M) = C5H8-13E+CH3(+M) 3.39E+11 0.66 32262.9 ! Refa to S3XC6H11-1E(+M) = C4H6+C2H5(+M)

LOW / 4.00E-42 18.05 -602.6 /

TROE / -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

! P6XC6H11-3E Come from C2H5-3-PXC6H10

PXCH2-3-1C5H9(+M) = C4H6+C2H5(+M) 4.90E+12 0.15 11139.1 ! 08/TSAwip

LOW / 1.70E-14 9.652 -603.1/

TROE / -76.60 221 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

! reactions of C2H3cC5H9 (C7H12)

C2H3cC5H9=C7H12-13E 2.45E20 -0.97 92860 ! Sirjean 2006 cyclopentane hpl, J. Phys. Chem. A 110 (2006) 12693-12704

PLOG / 0.039 1.25E19 -0.97 92860 / ! EST /20

PLOG / 1.0 2.45E20 -0.97 92860 / !

C2H3cC5H9+H = C2H3TXcC5H8+H2 2.65E+6 2.2 0.0 ! allylt LLNL-MI-407571

C2H3cC5H9+CH3 = C2H3TXcC5H8+CH4 4.613 3.1 2330 ! allylt LLNL-MI-407571

C2H3cC5H9+H = C2H3S2XcC5H8+H2 2.60E+06 2.4 4471 ! secondary LLNL-MI-407571 x2

C2H3cC5H9+CH3 = C2H3S2XcC5H8+CH4 3.02E+00 3.46 5481 ! secondary LLNL-MI-407571 x2

C2H3cC5H9+H = C2H3S3XcC5H8+H2 2.60E+06 2.4 4471 ! secondary LLNL-MI-407571 x2

C2H3cC5H9+CH3 = C2H3S3XcC5H8+CH4 3.02E+00 3.46 5481 ! secondary LLNL-MI-407571 x2

C2H3TXcC5H8=C2H3-2-PXC5H8 1.86E+12 0.419 34370 ! 1-methylcyclopentyl radical sirjean 2008 hpl, J. Phys. Chem. A 112 (2008) 11598-11610

PLOG / 0.039 0.93E+11 0.419 34370 / ! EST /20

PLOG / 1.0 1.86E+12 0.419 34370 / !

C2H3-2-PXC5H8(+M) = P1XCH2C4H5-13E+C2H4(+M) 4.57E+12 0.13 24386.4 ! Refa S5XC6H11-1E(+M) = C3H6+aC3H5(+M)

LOW / 2.50E-31 14.57 -578.8 /

TROE / -13.17 268 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

! to reduce the complex, only the ring opening to linear products were considered at present! reactions of C2H3cC5H9 (C7H12)

C2H3cC5H9=C7H12-13E 2.45E20 -0.97 92860 ! Sirjean 2006 cyclopentane hpl, J. Phys. Chem. A 110 (2006) 12693-12704

PLOG / 0.039 1.25E19 -0.97 92860 / ! EST /20

PLOG / 1.0 2.45E20 -0.97 92860 / !

C2H3cC5H9+H = C2H3TXcC5H8+H2 2.65E+6 2.2 0.0 ! allylt LLNL-MI-407571

C2H3cC5H9+CH3 = C2H3TXcC5H8+CH4 4.613 3.1 2330 ! allylt LLNL-MI-407571

C2H3cC5H9+H = C2H3S2XcC5H8+H2 2.60E+06 2.4 4471 ! secondary LLNL-MI-407571 x2

C2H3cC5H9+CH3 = C2H3S2XcC5H8+CH4 3.02E+00 3.46 5481 ! secondary LLNL-MI-407571 x2

C2H3cC5H9+H = C2H3S3XcC5H8+H2 2.60E+06 2.4 4471 ! secondary LLNL-MI-407571 x2

C2H3cC5H9+CH3 = C2H3S3XcC5H8+CH4 3.02E+00 3.46 5481 ! secondary LLNL-MI-407571 x2

C2H3TXcC5H8=C2H3-2-PXC5H8 1.86E+12 0.419 34370 ! 1-methylcyclopentyl radical sirjean 2008 hpl, J. Phys. Chem. A 112 (2008) 11598-11610

PLOG / 0.039 0.93E+11 0.419 34370 / ! EST /20

PLOG / 1.0 1.86E+12 0.419 34370 / !

C2H3-2-PXC5H8(+M) = P1XCH2C4H5-13E+C2H4(+M) 4.57E+12 0.13 24386.4 ! Refa S5XC6H11-1E(+M) = C3H6+aC3H5(+M)

LOW / 2.50E-31 14.57 -578.8 /

TROE / -13.17 268 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

! to reduce the complex, only the ring opening to linear products were considered at present

C2H3S2XcC5H8=P7XC7H11-13E 4.27E+12 0.404 33710 ! 2-methylcyclopentyl radical sirjean 2008 hpl, J. Phys. Chem. A 112 (2008) 11598-11610

PLOG / 0.039 2.15E+11 0.404 33710 / ! EST /20

PLOG / 1.0 4.27E+12 0.404 33710/ !

C2H3S3XcC5H8=S3XC7H11-16E 1.44E+13 0.277 33740 ! 3-methylcyclopentyl radical sirjean 2008 hpl, J. Phys. Chem. A 112 (2008) 11598-11610

PLOG / 0.039 0.75E+12 0.277 33740 / ! EST /20

PLOG / 1.0 1.44E+13 0.277 33740/ !

P7XC7H11-13E(+M) = lC5H7+C2H4(+M) 4.57E+12 0.13 24386.4 ! Refa S5XC6H11-1E(+M) = C3H6+aC3H5(+M)

LOW / 2.50E-31 14.57 -578.8 /

TROE / -13.17 268 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

!reactions of PAXCH2-2-1C6H11 (C7H13)

! PAXCH2-2-1C6H11 come from C2H5-2-1C6H11

PAXCH2-2-1C6H11 = aC3H4+pC4H9 2.00E+13 0.00 50078.0 !

PLOG / 0.039 1.00E+12 0.00 50078.0 / ! /20 EST

PLOG / 1.0E+5 2.00E+13 0.00 50078.0 / ! 73/TSA JetSurF 2.0

! reactions of C8H12 chain dienes

! C2H3-2-1C6H11 come from CH3CH-2-1C6H11

C2H3-2-1C6H11=P1XCH2C4H5-13E+nC3H7 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7

! PLOG / 0.039 1.07E+80 -19.33 95177/ !

PLOG / 0.066 2.50E+68 -16.040 86832/ !

PLOG / 0.132 1.480E+59 -13.261 82596/ !

PLOG / 0.197 2.43E+61 -13.999 82637/ !

PLOG / 0.263 3.75E+59 -13.427 82179/ !

PLOG / 1.0E+5 1.46E+16 0.00 69120/ !

!reactions of cyclic C8H9

! CH2CH-1-SAXcC6H6 CH2CH-2-SAXcC6H6 CH2CH-3-SAXcC6H6 CH2CH-4-SAXcC6H6

CH2CH-5-SAXcC6H6

CH2CH-1-SAXcC6H6(+M)= A1C2H3+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1/

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

CH2CH-2-SAXcC6H6(+M)= A1C2H3+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1/

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

CH2CH-3-SAXcC6H6(+M)= A1C2H3+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1/

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

CH2CH-4-SAXcC6H6(+M)= A1C2H3+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1/

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

CH2CH-5-SAXcC6H6(+M)= A1C2H3+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1/

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

! reactions of cyclic C8H10

! CH2CH-1-cC6H7-13 CH2CH-2-cC6H7-13 CH3CH-5-cC6H6-13 CH3CH-3-cC6H6-14

CH2CH-1-cC6H7-13+H = CH2CH-1-SAXcC6H6+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

CH2CH-1-cC6H7-13+CH3 = CH2CH-1-SAXcC6H6+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

CH2CH-1-SAXcC6H6+H(+M)=CH2CH-1-cC6H7-13(+M) 1.33E+13 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *2/3

LOW / 0.89E+59 -12.00 5967.8 /

TROE/ 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

CH2CH-1-cC6H7-13+H = CH2CH-4-SAXcC6H6+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

CH2CH-1-cC6H7-13+CH3 = CH2CH-4-SAXcC6H6+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

CH2CH-4-SAXcC6H6+H(+M)=CH2CH-2-cC6H7-13(+M) 1.33E+13 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *2/3

LOW / 0.89E+59 -12.00 5967.8 /

TROE/ 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

CH2CH-2-cC6H7-13+H = CH2CH-2-SAXcC6H6+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

CH2CH-2-cC6H7-13+CH3 = CH2CH-2-SAXcC6H6+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

CH2CH-2-SAXcC6H6+H(+M)=CH2CH-2-cC6H7-13(+M) 1.33E+13 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *2/3

LOW / 0.89E+59 -12.00 5967.8 /

TROE/ 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

CH2CH-2-cC6H7-13+H = CH2CH-3-SAXcC6H6+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

CH2CH-2-cC6H7-13+CH3 = CH2CH-3-SAXcC6H6+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

CH2CH-3-SAXcC6H6+H(+M)=CH2CH-2-cC6H7-13(+M) 1.33E+13 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *2/3

LOW / 0.89E+59 -12.00 5967.8 /

TROE/ 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

!reactions of cyclic C8H11

CH2CH-2-SAXcC6H8(+M)=CH2CH-2-cC6H7-13+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1/

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

CH2CH-1-SAXcC6H8(+M)=CH2CH-1-cC6H7-13+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1/

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

C2H5-1-SAXcC6H6(+M)=A1C2H5+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1/

TROE / -51.87 258 28 50000.0 /

```
H2/2/ CH4/2/ C2H6/3/
C2H5-4-SAXcC6H6(+M)=A1C2H5+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3
LOW / 3.07E-37 15.37 -603.1/
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
CH3CH-1-cC6H7-13(+M)=CH2CH-1-cC6H7-13+H(+M) 4.70E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M)
LOW/ 4.61E-37 15.37 -603.1 /
TROE/ -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
C2H5-3-SAXcC6H6(+M)= A1C2H5+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3
LOW / 3.07E-37 15.37 -603.1/
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
C2H5-2-SAXcC6H6(+M)= A1C2H5+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3
LOW / 3.07E-37 15.37 -603.1/
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
CH3CH-2-cC6H7-13(+M)= CH2CH-2-cC6H7-13+H(+M) 4.70E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M)
LOW / 4.6E-37 15.37 -603.1/
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
C2H5-6-SAXcC6H6(+M)=A1C2H5+H(+M) 1.56E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *1/3
LOW / 1.53E-37 15.37 -603.1/
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
C2H5-6-SAXcC6H6=A1+C2H5 4.24E+21 -3.89 22867 ! 800 K-2000 K ref to S2XMCH=cC6H10+CH3
PLOG / 0.039 4.24E+21 -3.89 22867/
PLOG / 0.197 2.58E+22 -3.86 24360/
PLOG / 1.000 2.27E+28 -5.30 29571/
PLOG / 10.000 4.14E+38 -7.84 39088/
PLOG / 100.000 1.94E+45 -9.36 47105/
PLOG / 1.0E+5 6.35E+13 0.20 33524/
```

C2H5-5-SAXcC6H6(+M)=A1C2H5+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1/

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

C2H5-5-SAXcC6H6(+M)=CH2cC6H6-13E+CH3(+M) 3.39E+11 0.66 32262.9 ! Ref to S3XC6H11-1E(+M) = C4H6+C2H5(+M)

LOW / 4.00E-42 18.05 -602.6/

TROE / -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

! reactions of cyclic C8H12

C2H5-1-cC6H7-13+H = C2H5-1-SAXcC6H6+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C2H5-1-cC6H7-13+CH3 = C2H5-1-SAXcC6H6+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C2H5-1-SAXcC6H6+H(+M)=C2H5-1-cC6H7-13(+M) 1.33E+14 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M *2/3

LOW / 0.89E+60 -12.00 5967.8 /

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C2H5-1-cC6H7-13+H = C2H5-4-SAXcC6H6+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C2H5-1-cC6H7-13+CH3 = C2H5-4-SAXcC6H6+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C2H5-4-SAXcC6H6 + H(+M) = C2H5-1-cC6H7-13(+M) 1.33E+14 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M *2/3

LOW / 0.89E+60 -12.00 5967.8 /

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C2H5-1-cC6H7-13+H = CH3CH-1-cC6H7-13+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C2H5-1-cC6H7-13+CH3 = CH3CH-1-cC6H7-13+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

CH3CH-1-cC6H7-13 + H(+M) = C2H5-1-cC6H7-13(+M) 1.33E+14 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M *2/3

LOW / 0.89E+60 -12.00 5967.8 /

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

CH2S4XcC6H7-5E+CH3(+M)=C2H5-1-cC6H7-13 (+M) 1.00E+14 -0.32 -262. ! Ref to aC3H5+CH3(+M)=C4H8-1(+M)

LOW / 3.51E+60 -12.97 6000./

TROE / 0.896 60000 1606 6118/

H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/

C2H5-2-cC6H7-13+H = C2H5-3-SAXcC6H6+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C2H5-2-cC6H7-13+CH3 = C2H5-3-SAXcC6H6+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C2H5-3-SAXcC6H6+H(+M)=C2H5-2-cC6H7-13(+M) 1.33E+13 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *2/3

LOW / 0.89E+59 -12.00 5967.8 /

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C2H5-2-cC6H7-13+H = C2H5-2-SAXcC6H6+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C2H5-2-cC6H7-13+CH3 = C2H5-2-SAXcC6H6+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C2H5-2-SAXcC6H6+H(+M)=C2H5-2-cC6H7-13(+M) 1.33E+13 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *2/3

LOW / 0.89E+59 -12.00 5967.8/

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C2H5-2-cC6H7-13+H = CH3CH-2-cC6H7-13+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C2H5-2-cC6H7-13+H = CH3CH-2-cC6H7-13+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C2H5-2-cC6H7-13+CH3 = CH3CH-2-cC6H7-13+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

CH3CH-2-cC6H7-13+H(+M)=C2H5-2-cC6H7-13(+M) 1.33E+13 0.00 0.0 !ref to aC3H5+H(+M) = C3H6(+M) *2/3

LOW / 0.89E+59 -12.00 5967.8 /

TROE/ 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/CH3CH-2-cC6H7-13+H(+M)=C2H5-2-cC6H7-13(+M) 1.33E+13 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/3

LOW / 0.89E+59 -12.00 5967.8 /

TROE/ 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

CH2S2XcC6H7-5E+CH3(+M)=C2H5-2-cC6H7-13 (+M) 1.00E+14 -0.32 -262. ! Refa to aC3H5+CH3(+M)=C4H8-1(+M)

LOW / 3.51E+60 -12.97 6000./

TROE / 0.896 60000 1606 6118/

H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/

C2H5-5-cC6H7-13+H = C2H5-6-SAXcC6H6+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C2H5-5-cC6H7-13+CH3 = C2H5-6-SAXcC6H6+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C2H5-6-SAXcC6H6+H(+M)=C2H5-5-cC6H7-13(+M) 1.33E+13 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/3

LOW / 0.89E+59 -12.00 5967.8/

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C2H5-5-cC6H7-13+H = C2H5-5-SAXcC6H6+H2 2.65E+6 2.2 0.0 ! allylt LLNL-MI-407571

C2H5-5-cC6H7-13+CH3 = C2H5-5-SAXcC6H6+CH4 4.613 3.1 2330 ! allylt LLNL-MI-407571

C2H5-5-SAXcC6H6+H(+M)=C2H5-5-cC6H7-13(+M) 0.67E+13 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *1/3

LOW / 0.44E+59 -12.00 5967.8/

TROE/ 0.020 1096.6 1096.6 6859.5/

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S1XcC6H7-24E+C2H5(+M)=C2H5-5-cC6H7-13 (+M) 1.00E+14 -0.32 -262. ! Refa to aC3H5+CH3(+M)=C4H8-1(+M)

LOW / 3.51E+60 -12.97 6000./

TROE / 0.896 60000 1606 6118/

H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/

! reactions of C2H3-2-PXC6H10, PXC8H13-13, C2H3-3-PXC6H10, SAXC8H13-17, C2H3-4-PXC6H10, C2H3-5-PXC6H10

C2H3-2-PXC6H10(+M) = C2H3-2-PXC4H6+C2H4(+M) 3.98E+12 0.12 27571.6 ! Refa to P6XC6H11-1E(+M) = C4H7+C2H4(+M)

LOW / 3.30E-43 18.35 -602.5 /

TROE / -13.87 227 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

PXC8H13-13(+M) = P6XC6H9-13E+C2H4(+M) 3.98E+12 0.12 27571.6 ! Refa to P6XC6H11-1E(+M) = C4H7+C2H4(+M)

LOW / 3.30E-43 18.35 -602.5 /

TROE / -13.87 227 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C2H3-3-PXC6H10(+M) = C2H3-3-PXC4H6+C2H4(+M) 3.98E+12 0.12 27571.6 ! Refa to P6XC6H11-1E(+M) = C4H7+C2H4(+M)

LOW / 3.30E-43 18.35 -602.5 /

TROE / -13.87 227 28 50000.0 /

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H2/2/ CH4/2/ C2H6/3/ AR/0.7/
SAXC8H13-17(+M) = C4H6+C4H7(+M) 3.39E+11 0.66 32262.9 ! Refa to S3XC6H11-1E(+M) = C4H6+C2H5(+M)
LOW / 4.00E-42 18.05 -602.6 /
TROE / -18.50 246 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C2H3-4-PXC6H10(+M) = S3XC6H9-15E+C2H4(+M) 3.98E+12 0.12 27571.6 ! Refa to P6XC6H11-1E(+M) = C4H7+C2H4(+M)
LOW / 3.30E-43 18.35 -602.5 /
TROE / -13.87 227 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C2H3-5-PXC6H10(+M) = C4H6+C4H7(+M) 3.98E+12 0.12 27571.6 ! Refa to P6XC6H11-1E(+M) = C4H7+C2H4(+M)
LOW / 3.30E-43 18.35 -602.5 /
TROE / -13.87 227 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
! reactions of cyclic C8H13
!! CH2CH-1-cC6H10 reactions
CH2CH-1-cC6H10=C2H3-2-PXC6H10 7.77E+21 -3.78 22330 ! Refa to T1XMCH=P6XC6H10-1E2M
PLOG / 0.039 7.77E+21 -3.78 22330 / ! 800 K-2000 K
PLOG / 0.197 2.46E+23 -3.98 24528 / ! 800 K-2000 K
PLOG / 1.000 3.46E+31 -6.06 31348 / ! 800 K-2000 K
PLOG / 10.000 3.04E+40 -8.25 40204 / ! 800 K-2000 K
PLOG / 100.000 3.40E+43 -8.78 45692 / ! 800 K-2000 K
PLOG / 1.0E+5 2.51E+13 0.24 31344 / ! 800 K-2000 K
!! CH2CH-2-cC6H10 reactions
CH2CH-2-cC6H10=C2H3-3-PXC6H10 1.24E+22 -4.01 22066 ! Refa to S2XMCH=P6XC6H10-1E3M
PLOG / 0.039 1.24E+22 -4.01 22066 / ! 800 K-2000 K
PLOG / 0.197 4.17E+22 -3.93 23430 / ! 800 K-2000 K
PLOG / 1.000 1.01E+28 -5.23 28271 / ! 800 K-2000 K
PLOG / 10.000 2.14E+37 -7.54 37062 / ! 800 K-2000 K
PLOG / 100.000 1.11E+43 -8.81 44209 / ! 800 K-2000 K
PLOG / 1.0E+5 1.59E+13 0.22 31118 / ! 800 K-2000 K
CH2CH-2-cC6H10=PXC8H13-13 2.99E+22 -4.04 21843 ! Refa to S2XMCH=P7XC7H13-2E
PLOG / 0.039 2.99E+22 -4.04 21843 / ! 800 K-2000 K
PLOG / 0.197 8.66E+22 -3.95 23164 / ! 800 K-2000 K
PLOG / 1.000 1.44E+28 -5.21 27888 / ! 800 K-2000 K
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    PLOG / 10.000 1.61E+37 -7.45 36452 / ! 800 K-2000 K
    PLOG / 100.000 4.39E+42 -8.66 43334 / ! 800 K-2000 K
    PLOG / 1.0E+5 2.37E+13 0.19 30429 / ! 800 K-2000 K
    !! CH2CH-3-cC6H10 reactions
    CH2CH-3-cC6H10=C2H3-4-PXC6H10 1.21E+18 -2.84 19903 ! Refa to S3XMCH=P6XC6H10
1E4M
    PLOG / 0.039 1.21E+18 -2.84 19903 / ! 800 K-2000 K
    PLOG / 0.197 7.98E+21 -3.70 23365 / ! 800 K-2000 K
    PLOG / 1.000 2.52E+28 -5.31 28978 / ! 800 K-2000 K
    PLOG / 10.000 8.05E+37 -7.66 38033 / ! 800 K-2000 K
    PLOG / 100.000 6.13E+42 -8.70 44718 / ! 800 K-2000 K
    PLOG / 1.0E+5 1.68E+13 0.21 31241 / ! 800 K-2000 K
    CH2CH-3-cC6H10=SAXC8H13-17 5.23E+18 -2.93 19555 ! Refa to S3XMCH=S6XC7H13-
1E
    PLOG / 0.039 5.23E+18 -2.93 19555 / ! 800 K-2000 K
    PLOG / 0.197 2.06E+22 -3.73 22876 / ! 800 K-2000 K
    PLOG / 1.000 3.29E+28 -5.27 28275 / ! 800 K-2000 K
    PLOG / 10.000 3.31E+37 -7.49 36918 / ! 800 K-2000 K
    PLOG / 100.000 8.80E+41 -8.42 43157 / ! 800 K-2000 K
    PLOG / 1.0E+5 2.55E+13 0.17 30061 / ! 800 K-2000 K
    !! CH2CH-4-cC6H10 reactions
    CH2CH-4-cC6H10=C2H3-5-PXC6H10 1.26E+22 -3.85 22627 ! Refa to S4XMCH=P6XC6H10
1E5M
    PLOG / 0.039 1.26E+22 -3.85 22627 / ! 800 K-2000 K
    PLOG / 0.197 3.57E+26 -4.89 26638 / ! 800 K-2000 K
    PLOG / 1.000 2.59E+32 -6.32 32020 / ! 800 K-2000 K
    PLOG / 10.000 2.07E+41 -8.51 40814 / ! 800 K-2000 K
    PLOG / 100.000 5.79E+44 -9.15 46530 / ! 800 K-2000 K
    PLOG / 1.0E+5 3.87E+13 0.20 31782 / ! 800 K-2000 K
    C2H5-1-SAXcC6H8(+M)=C2H5-1-cC6H7-13+H(+M) 3.13E+08 1.32 44697.6
! Refa to SAXC4H7(+M) = C4H6+H(+M *2/3
    LOW/ 3.07E-37 15.37 -603.1/
    TROE / -51.87 258 28 50000.0 /
    H2/2/ CH4/2/ C2H6/3/
    C2H5-2-SAXcC6H8(+M)=C2H5-2-cC6H7-13+H(+M) 3.13E+08 1.32 44697.6
! Refa to SAXC4H7(+M) = C4H6+H(+M *2/3
    LOW / 3.07E-37 15.37 -603.1/
    TROE/ -51.87 258 28 50000.0 /
    H2/2/ CH4/2/ C2H6/3/
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C2H5-6-SAXcC6H8(+M)=C2H5-5-cC6H7-13+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M *2/3
LOW/ 3.07E-37 15.37 -603.1/
TROE /-51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
C2H5-3-SAXcC6H8(+M)=C2H5-2-cC6H7-13+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M *2/3
LOW / 3.07E-37 15.37 -603.1/
TROE/ -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
C2H5-3-SAXcC6H8=CH2cC6H8-2E+CH3 1.17E+22 -3.78 22330 ! EST, C2H5TXcC6H10=C2H5-2-PXC6H10 *1.5, fall off from C2H5TXcC6H10=C2H5-2-PXC6H10.
PLOG / 0.039 1.17E+22 -3.78 22330 /
PLOG / 0.197 3.69E+23 -3.98 24528 /
PLOG / 1.000 5.19E+31 -6.06 31348 /
PLOG / 10.000 4.56E+40 -8.25 40204 /
PLOG / 100.000 5.10E+43 -8.78 45692 /
PLOG / 1.0E+5 3.77E+13 0.24 31344 /
C2H5-4-SAXcC6H8=cC6H8-13E+C2H5 1.06E+22 -3.89 22867 ! 800 K-2000 K refa to C2H5S2XcC6H10=cC6H10+C2H5
PLOG / 0.039 1.06E+22 -3.89 22867 /
PLOG / 0.197 6.45E+22 -3.86 24360 /
PLOG / 1.000 5.68E+28 -5.30 29571 /
PLOG / 10.000 1.04E+39 -7.84 39088 /
PLOG / 100.000 4.85E+45 -9.36 47105 /
PLOG / 1.0E+5 1.59E+14 0.20 33524 /
C2H5-4-SAXcC6H8=C2H5-1-cC6H7-13+H 2.06E+20 -3.80 23117 ! 800 K-2000 K refa to S2XMCH=MCH-1E+H
PLOG / 0.039 2.06E+20 -3.80 23117 /
PLOG / 0.197 1.50E+21 -3.78 24651 /
PLOG / 1.000 2.14E+27 -5.27 30013 /
PLOG / 10.000 8.88E+37 -7.90 39841 /
PLOG / 100.000 9.49E+44 -9.50 48246 /
PLOG / 1.0E+5 5.69E+11 0.60 34004 /
C2H5-5-SAXcC6H8(+M)=C2H5-5-cC6H7-13+H(+M) 3.13E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M *2/3
LOW/ 3.07E-37 15.37 -603.1/
TROE/ -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
!reactions of C8H14-13E
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C8H14-13E+H = C6H12-1E+C2H3 1.46E+30 -4.34 21647.0 ! =(C4H6+H)

C8H14-13E= nC3H7+lC5H7 1.07E+80 -19.33 95177 ! Refa to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

! reactions of cyclic C8H14

! CH2CHcC6H11 reactions CH2CHcC6H11=C8H14-13E 1.00 0.00 0.00 ! Refa to MCH = C7H14-2E, without considering the allylic resonance

PLOG / 0.01 9.52E+114 -28.98 140737 /

PLOG / 0.0395 1.74E+103 -25.40 135829 /

PLOG / 0.197 3.34E+87 -20.68 128511 /

PLOG / 0.395 5.32E+79 -18.37 124487 /

PLOG / 1 9.66E+68 -15.21 118735 /

PLOG / 10 8.51E+43 -7.89 104630 /

PLOG / 100 1.38E+26 -2.74 94184 /

PLOG / 1.0E+5 1.90E+16 0.12 88289 /

CH2CH-1-cC6H10+H(+M) = CH2CHcC6H11(+M) 2.00E+14 0.00 0.0 ! EST From C4H8-1

LOW / 2.66E+60 -12.00 5967.8 /

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

CH2CHcC6H11+H = CH2CH-1-cC6H10+H2 2.65E6 2.2 0.0 ! allylt LLNL-MI-407571

CH2CHcC6H11+CH3 = CH2CH-1-cC6H10+CH4 4.613 3.1 2330 ! allylt LLNL-MI-407571

CH2CHcC6H11+H=CH2CH-2-cC6H10+H2 1.3E06 2.4 4471 ! secondary LLNL-MI-407571

CH2CHcC6H11+CH3=CH2CH-2-cC6H10+CH4 1.51 3.46 5481 ! secondary LLNL-MI-407571

CH2CHcC6H11+H=CH2CH-3-cC6H10+H2 1.3E06 2.4 4471 ! secondary LLNL-MI-407571

CH2CHcC6H11+CH3=CH2CH-3-cC6H10+CH4 1.51 3.46 5481 ! secondary LLNL-MI-407571

CH2CHcC6H11+H=CH2CH-4-cC6H10+H2 1.3E06 2.4 4471 ! secondary LLNL-MI-407571

CH2CHcC6H11+CH3=CH2CH-4-cC6H10+CH4 1.51 3.46 5481 ! secondary LLNL-MI-407571

! CH3CHcC6H10 reactions

CH3CHcC6H10+H = CH2CH-1-cC6H10+H2 1.73E5 2.5 2492 ! allylp LLNL-MI-407571

CH3CHcC6H10+CH3 = CH2CH-1-cC6H10+CH4 2.2098 3.5 5675 ! allylp LLNL-MI-407571

CH2CH-1-cC6H10+H(+M)=CH3CHcC6H10(+M) 2.00E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M)

LOW / 1.35E+60 -12.00 5967.8 /

TROE/ 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

! C2H5-1-cC6H9 reactions

C2H5-1-cC6H9+H = C2H5-1-SAXcC6H8+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C2H5-1-cC6H9+CH3 = C2H5-1-SAXcC6H8+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C2H5-1-SAXcC6H8+H(+M)=C2H5-1-cC6H9(+M) 1.33E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/3

LOW/ 0.90E+60 -12.00 5967.8 /

TROE /0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C2H5-1-cC6H9+H = C2H5-2-SAXcC6H8+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C2H5-1-cC6H9+CH3 = C2H5-2-SAXcC6H8+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C2H5-2-SAXcC6H8+H(+M) = C2H5-1-cC6H9(+M) 1.33E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/3

LOW/ 0.90E+60 -12.00 5967.8 /

TROE /0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C2H5-1-cC6H9+H = CH3CH-1-cC6H9+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C2H5-1-cC6H9+CH3 = CH3CH-1-cC6H9+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

CH3CH-1-cC6H9+H(+M) = C2H5-1-cC6H9(+M) 1.33E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/3

LOW/ 0.90E+60 -12.00 5967.8 /

TROE /0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

CH2S2XcC6H9+CH3(+M)=C2H5-1-cC6H9(+M) 1.00E+14 -0.32 -262. ! Refa to aC3H5+CH3(+M)=C4H8-1(+M)

LOW / 3.51E+60 -12.97 6000./

TROE / 0.896 60000 1606 6118/

H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/

! C2H5-3-cC6H9 reactions

C2H5-3-cC6H9+H = C2H5-6-SAXcC6H8+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C2H5-3-cC6H9+CH3 = C2H5-6-SAXcC6H8+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C2H5-6-SAXcC6H8+H(+M)=C2H5-3-cC6H9(+M) 1.33E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/3

LOW/ 0.90E+60 -12.00 5967.8 /

TROE /0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C2H5-3-cC6H9+H = C2H5-3-SAXcC6H8+H2 2.65E+6 2.2 0.0 ! allylt LLNL-MI-407571

C2H5-3-cC6H9+CH3 = C2H5-3-SAXcC6H8+CH4 4.613 3.1 2330 ! allylt LLNL-MI-407571

C2H5-3-SAXcC6H8+H(+M)=C2H5-3-cC6H9(+M) 0.67E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) /3

LOW / 0.44E+60 -12.00 5967.8 /

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S3XcC6H9-1E+C2H5(+M)=C2H5-3-cC6H9 (+M) 1.00E+14 -0.32 -262. ! RefA to aC3H5+CH3(+M)=C4H8-1(+M) Tsang 91

LOW / 3.5E+60 -12.97 6000./

TROE / 0.896 60000 1606 6118/

H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/

C2H5-3-cC6H9=C6H10-13E+C2H4 5.0E+78 -18.94 98386 ! refa to cC6H10 = C4H6+C2H4

PLOG / 0.039 5.0E+78 -18.94 98386 /

PLOG / 0.197 2.60E+70 -16.36 95510 /

PLOG / 1.0 3.81E+25 -3.58 64034 /

PLOG / 1.0E+5 8.31E+13 0.387 64116 /

! C2H5-4-cC6H9 reactions

C2H5-4-cC6H9+H = C2H5-4-SAXcC6H8+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C2H5-4-cC6H9+CH3 = C2H5-4-SAXcC6H8+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C2H5-4-SAXcC6H8+H(+M)=C2H5-4-cC6H9(+M) 1.33E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/3

```
LOW / 0.90E+60 -12.00 5967.8 /
TROE / 0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C2H5-4-cC6H9+H = C2H5-5-SAXcC6H8+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571
C2H5-4-cC6H9+CH3 = C2H5-5-SAXcC6H8+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
C2H5-5-SAXcC6H8+H(+M)=C2H5-4-cC6H9(+M) 1.33E+14 0.00 0.0 ! Refa to aC3H5+H(+M) = C3H6(+M) *2/3
LOW / 0.90E+60 -12.00 5967.8 /
TROE/ 0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C2H5-4-cC6H9=C4H8-1+C4H6 5.0E+78 -18.94 98386 ! refa to cC6H10 = C4H6+C2H4
PLOG / 0.039 5.0E+78 -18.94 98386 /
PLOG / 0.197 2.60E+70 -16.36 95510 /
PLOG / 1.0 3.81E+25 -3.58 64034 /
PLOG / 1.0E+5 8.31E+13 0.387 64116 /
C2H5-4-cC6H9 = S3XcC6H9-1E+C2H5 1.00 0.00 0.00 ! Refa to MCH = cC6H11+CH3
PLOG / 0.01 1.85E+105 -26.15 129214 /
PLOG / 0.0395 1.19E+92 -22.23 122595 /
PLOG / 0.197 1.50E+80 -18.67 116938 /
PLOG / 0.395 8.65E+63 -13.89 108211 /
PLOG / 1 5.93E+64 -14.15 108486 /
PLOG / 10 3.59E+45 -8.56 97430 /
PLOG / 100 1.66E+33 -4.99 90100 /
PLOG / 1.0E+5 1.10E+27 -3.20 86385 /
! C8H15 alkenyl reactions
!!! P8XC8H15-2E reaction
P8XC8H15-2E(+M) = P6XC6H11-2E+C2H4(+M) 3.98E+12 0.12 27571.6 ! Refa to P6XC6H11-1E(+M) = C4H7+C2H4(+M)
LOW / 3.30E-43 18.35 -602.5 /
TROE / -13.87 227 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
P8XC8H15-2E(+M) = S4XC8H15-2E(+M) 2.29E+01 2.82 10755.6 ! Refa to PXC8H17(+M) = S3XC8H17(+M), 1,5-H shift, without consideration of allylic resonance, in JetSurF 2.0
LOW / 9.90E-38 17.215 -603.0 /
TROE / -16.33 200.0 28.0 5000000 /
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H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S4XC8H15-2E(+M) = C5H8-13E+nC3H7(+M) 3.39E+11 0.66 32262.9 ! Refa to S3XC6H11-1E(+M) = C4H6+C2H5(+M)
LOW / 4.00E-42 18.05 -602.6 /
TROE / -18.50 246 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S4XC8H15-2E(+M) = C8H14-13E+H(+M) 4.70E+08 1.32 44697.6 ! Refa to SAXC4H7(+M) = C4H6+H(+M)
LOW / 4.6E-37 15.37 -603.1/
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
! P7XC7H12-1E3M reaction
P7XC7H12-1E3M(+M) = P5XC5H8-1E3M+C2H4(+M) 3.98E+12 0.12 27571.6 !ref to P6XC6H11-1E(+M) = C4H7+C2H4(+M)
LOW / 3.30E-43 18.35 -602.5 /
TROE / -13.87 227 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
P7XC7H12-1E3M(+M) = T3XC7H12-1E3M(+M) 2.29E+01 2.82 10755.6 ! est
LOW / 9.90E-38 17.215 -603.0 /
TROE / -16.33 200.0 28.0 5000000 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
T3XC7H12-1E3M(+M) = C4H5-13E2M+nC3H7(+M) 3.39E+11 0.66 32262.9 !ref to S3XC6H11-1E(+M) = C4H6+C2H5(+M)
LOW / 4.00E-42 18.05 -602.6 /
TROE / -18.50 246 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
!!! C2H5-2-PXC6H10 reaction
C2H5-2-PXC6H10(+M) = PXC2H4-2-1C4H7+C2H4(+M) 3.98E+12 0.12 27571.6 !ref to P6XC6H11-1E(+M) = C4H7+C2H4(+M)
LOW / 3.30E-43 18.35 -602.5 /
TROE / -13.87 227 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C2H5-2-PXC6H10(+M) = C2H5-2-SAX1C6H10(+M) 1.55E+02 2.83 15566.2 !ref to P6XC6H11-1E(+M) = S3XC6H11-1E(+M)
LOW / 1.50E-30 14.56 -602.4 /
TROE / -13.59 214 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
!! CH3CH-2-1C6H11 reaction
C2H5-2-PXC6H10(+M) = CH3CH-2-1C6H11(+M) 2.95E+00 3.08 11015.9 !ref to PXC8H17(+M) = S2XC8H17(+M) 1,6-H shift,without consideration of allylic
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resonance, in JetSurF 2.0
    LOW / 3.90E-34 15.855 -606.2 /
    TROE / -15.24 216.0 28.0 5000000 /
    H2/2/ CH4/2/ C2H6/3/ AR/0.7/
    CH3CH-2-1C6H11(+M) = C2H3-2-1C6H11+H(+M) 4.70E+08 1.32 44697.6
!ref to SAXC4H7(+M) = C4H6+H(+M)
    LOW / 4.6E-37 15.37 -603.1/
    TROE / -51.87 258 28 50000.0 /
    H2/2/ CH4/2/ C2H6/3/
    CH3CH-2-1C6H11 = C4H612+pC4H9 7.10E+10 1.38 56360 !ref to iC4H7=aC3H4+CH3,
HPL, 2005 Zheng et al. J. Phys. Chem. A, 109 (2005) 9044 - 9053
    PLOG / 0.039 3.55E+09 1.38 56360 / ! EST/20
    PLOG / 1.0 7.10E+10 1.38 56360 /
    !!! C2H5-3-PXC6H10 reaction
    ! not refer to pxc6h11 C2H5-3-PXC6H10(+M) = PXCH2-3-1C5H9+C2H4(+M)
9.12E+11 0.31 27237.8 ! 08TSAb JetSurF 2.0
    LOW / 1.80E-57 23.463 -602.4/
    TROE / -2.46 206.0 28.0 50000.0 /
    H2/2/ CH4/2/ C2H6/3/ AR/0.7/
    C2H5-3-PXC6H10(+M) = C2H5-3-TAX1C6H10(+M) 8.60E+01 2.62 8722.9 !
08TSAc & Est-2 JetSurF 2.0
    LOW / 8.10E-33 15.214 -677.4 /
    TROE / -30.39 206.0 28.0 50000.0 /
    H2/2/ CH4/2/ C2H6/3/ AR/0.7/
    C2H5-3-TAX1C6H10(+M) = CH2-3-C6H10-1E+CH3(+M) 3.39E+11 0.66 32262.9
!ref to S3XC6H11-1E(+M) = C4H6+C2H5(+M)
    LOW / 4.00E-42 18.05 -602.6 /
    TROE / -18.50 246 28 50000.0 /
    H2/2/ CH4/2/ C2H6/3/ AR/0.7/
    !! C3H7-3-SXC5H8 reaction
    C2H5-3-PXC6H10(+M) = C3H7-3-SXC5H8(+M) 2.29E+01 2.82 10755.6 !ref
to PXC8H17(+M) = S3XC8H17(+M), 1,5-H shift, in JetSurF 2.0
    LOW / 9.90E-38 17.215 -603.0 /
    TROE / -16.33 200.0 28.0 5000000 /
    H2/2/ CH4/2/ C2H6/3/ AR/0.7/
    C3H7-3-SXC5H8(+M) = C5H8-13E+nC3H7(+M) 4.47E+11 0.57 28044.5 !
SXC6H13(+M) = C3H6+nC3H7(+M) in JetSurF 2.0
    LOW / 3.70E-33 14.91 -600.0 /
    TROE / -6.53 333.0 28.0 50000.0 /
    H2/2/ CH4/2/ C2H6/3/ AR/0.7/
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! C2H5-3-SXC6H10 reaction

C3H7-3-SXC5H8(+M) = C2H5-3-SXC6H10(+M) 1.41E+00 3.32 16144.4 !ref to SXC8H17(+M) = S3XC8H17(+M), 1,4-H shift in JetSurF 2.0

LOW / 5.20E-30 14.079 -606.4 /

TROE / -21.93 219.0 28.0 5000000 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C2H5-3-SXC6H10(+M) = S3XC5H9-1E+C3H6(+M) 4.57E+12 0.13 24386.4 ! Refa to S5XC6H11-1E(+M) = C3H6+aC3H5(+M) in JetSurF 2.0

LOW / 2.50E-31 14.57 -578.8 /

TROE / -13.17 268 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

! P8XC8H15-4E reaction

P8XC8H15-4E(+M) = S3XC6H11-1E+C2H4(+M) 4.57E+12 0.13 24386.4 ! Refa to S5XC6H11-1E(+M) = C3H6+aC3H5(+M) in JetSurF 2.0

LOW / 2.50E-31 14.57 -578.8 /

TROE / -13.17 268 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

P8XC8H15-4E(+M) = S5XC8H15-3E(+M) 2.95E+00 3.08 11015.9 ! Refa to PXC8H17(+M) = S2XC8H17(+M), 1,6-H shift, without consideration of allylic resonance, in JetSurF 2.0

LOW / 3.90E-34 15.855 -606.2/

TROE / -15.24 216.0 28.0 5000000 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

! C2H5-3-S2XC6H10 reaction

C2H5-3-S2XC6H10(+M) = C6H10-13E+C2H5(+M) 3.55E+12 0.29 28296.9 ! Refa to S2XC6H13(+M) = C2H5+C4H81(+M) in JetSurF 2.0

LOW / 4.50E-26 13.09 -600.5 /

TROE / -0.74 308.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

P8XC8H15-3E(+M) = P6XC6H11-3E+C2H4(+M) 9.12E+11 0.31 27237.8 ! 08TSAb

LOW / 1.80E-57 23.463 -602.4 /

TROE / -2.46 206.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

P8XC8H15-3E(+M) = S5XC8H15-3E(+M) 1.46E+11 0.00 10516.8 ! Est-2

LOW / 9.90E-38 17.215 -603.0 /

TROE / -16.33 200.0 28.0 5000000 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S5XC8H15-3E(+M) = C6H10-13E+C2H5(+M) 3.39E+11 0.66 32262.9 ! Refa to S3XC6H11-1E(+M) = C4H6+C2H5(+M)

LOW / 4.00E-42 18.05 -602.6 /

TROE / -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S5XC8H15-3E(+M) = C7H12-13E+CH3(+M) 3.39E+11 0.66 32262.9 ! Refa to S3XC6H11-1E(+M) = C4H6+C2H5(+M)

LOW / 4.00E-42 18.05 -602.6 /

TROE / -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

!!! reactions of PXC2H4-4-1C6H11

PXC2H4-4-1C6H11(+M) = S4XC6H11-1E+C2H4(+M) 3.98E+12 0.12 27571.6 ! Refa to P6XC6H11-1E(+M) = C4H7+C2H4(+M)

LOW / 3.30E-43 18.35 -602.5 /

TROE / -13.87 227 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

PXC2H4-4-1C6H11(+M) = C2H5-4-SAX1C6H10(+M) 1.55E+02 2.83 15566.2 ! Refa to P6XC6H11-1E(+M) = S3XC6H11-1E(+M)

LOW / 1.50E-30 14.56 -602.4 /

TROE / -13.59 214 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C2H5-4-SAX1C6H10(+M) = C6H10-13E+C2H5(+M) 3.39E+11 0.66 32262.9 ! Refa to S3XC6H11-1E(+M) = C4H6+C2H5(+M)

LOW / 4.00E-42 18.05 -602.6 /

TROE / -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

!!! reactions of C2H5-4-SXC6H10

PXC2H4-4-1C6H11(+M) = C2H5-4-SXC6H10(+M) 5.13E+00 3.23 16847.8 ! Refa to PXC8H17(+M) = S3XC8H17(+M), 1,4-H shift, in JetSurF 2.0

LOW / 5.10E-44 18.749 -602.9 /

TROE / -20.15 205.0 28.0 5000000 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C2H5-4-SXC6H10(+M) = C5H10-2E+aC3H5(+M) 4.57E+12 0.13 24386.4 ! Refa to S5XC6H11-1E(+M) = C3H6+aC3H5(+M)

LOW / 2.50E-31 14.57 -578.8 /

TROE / -13.17 268 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C2H5-4-SXC6H10(+M) = C6H10-14E+C2H5(+M) 1.76E+11 0.57 28791.6 ! Refa to 08TSAc (2-methyl-pent-4-yl)

LOW / 4.70E-39 16.77 -603.1/

TROE / -27.89 216 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

!!! reactions of S6XC8H15-1E

S6XC8H15-1E(+M) = C4H7+C4H8-1(+M) 2.04E+13 0.04 28493.6 ! Refa to S2XC8H17(+M) = pC4H9+C4H81(+M)

LOW / 3.00E-43 18.430 -602.8 /

TROE / -34.47 208.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S6XC8H15-1E(+M) = C7H12-16E+CH3(+M) 9.55E+09 1.08 29387.7 ! Refa to S2XC8H17(+M) = C7H14+CH3(+M)

LOW / 5.30E-46 19.133 -602.7 /

TROE / -34.36 210.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S6XC8H15-1E(+M) = S3XC8H15-1E(+M) 1.55E+02 2.83 15566.2 ! Refa to P6XC6H11-1E(+M) = S3XC6H11-1E(+M)

LOW / 1.50E-30 14.56 -602.4 /

TROE / -13.59 214 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S3XC8H15-1E(+M) = C4H6+pC4H9(+M) 3.39E+11 0.66 32262.9 ! Refa to S3XC6H11-1E(+M) = C4H6+C2H5(+M)

LOW / 4.00E-42 18.05 -602.6 /

TROE / -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S3XC8H15-1E(+M) = C8H14-13E+H(+M) 4.70E+08 1.32 44697.6 ! Refa to SAXC4H7 = C4H6 + H

LOW / 4.6E-37 15.37 -603.1/

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

!!! Reactions of PXCH2-5-1C7H13

PXCH2-5-1C7H13(+M) = C4H7+C4H8-1(+M) 1.76E+11 0.57 28791.6 ! 08TSAc

LOW / 4.70E-39 16.77 -603.1/

TROE / -27.89 216 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

PXCH2-5-1C7H13(+M) = C6H10-15E+C2H5(+M) 1.76E+11 0.57 28791.6 ! 08TSAc (2-methyl-pent-4-yl)

LOW / 4.70E-39 16.77 -603.1/

TROE / -27.89 216 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

PXCH2-5-1C7H13(+M) = S3XC7H12-1E5M(+M) 1.55E+02 2.83 15566.2 ! Refa to P6XC6H11-1E(+M) = S3XC6H11-1E(+M)

LOW / 1.50E-30 14.56 -602.4 /

TROE / -13.59 214 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S3XC7H12-1E5M(+M) = C4H6+sC4H9(+M) 3.39E+11 0.66 31262.9 ! Refa to S3XC6H11-1E(+M) = C4H6+C2H5(+M)

LOW / 4.00E-42 18.045 -602.6 /

TROE / -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

! Ethylcyclohexane radical reactions

PXC2H4cC6H11 = C2H5S2XcC6H10 4.58E+08 0.90 22900.0 ! 09/SI-WA JetSurF 2.0

PLOG / 0.039 2.29E+07 0.90 22900.0/ ! /20 EST

PLOG / 1.0 4.58E+08 0.90 22900.0/ !

PXC2H4cC6H11 = C2H5S3XcC6H10 4.94E+08 0.78 18644.0 ! 09/SI-WA JetSurF 2.0

PLOG / 0.039 2.47E+07 0.78 18644.0/ ! /20 EST

PLOG / 1.0 4.94E+08 0.78 18644.0/ !

PXC2H4cC6H11 = C2H5S4XcC6H10 7.97E+08 0.78 22740.0 ! 09/SI-WA JetSurF 2.0

PLOG / 0.039 4.00E+07 0.78 22740.0/ ! /20 EST

PLOG / 1.0 7.97E+08 0.78 22740.0/ !

SXC2H4cC6H11 = C2H5S3XcC6H10 4.65E+08 1.02 28687.0 ! 09/SI-WA JetSurF 2.0

PLOG / 0.039 2.33E+07 1.02 28687.0/ ! /20 EST

PLOG / 1.0 4.65E+08 1.02 28687.0/ !

SXC2H4cC6H11 = C2H5S4XcC6H10 1.19E+09 0.92 22700.0 ! 09/SI-WA JetSurF 2.0

PLOG / 0.039 5.95E+07 0.92 22700.0/ ! /20 EST

PLOG / 1.0 1.19E+09 0.92 22700.0/ !

PXC2H4cC6H11(+M) = cC6H11+C2H4(+M) 6.03E+10 0.84 27820.0 ! 08TSAb

LOW / 1.00E-43 18.591 -602.5/

TROE/ -43.32 200.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

CH2CHcC6H11+H(+M)=PXC2H4cC6H11(+M) 1.33E+13 0.00 3260.7 ! Refa to C3H6+H(+M) = nC3H7(+M)

LOW / 6.26E+38 -6.66 7000.0/

TROE/ 1.000 1000.0 1310.0 48097.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

SXC2H4cC6H11=P8XC8H15-2E 8.92E+18 -2.94 19897 ! Refa to PXCH2cC6H11=P7XC7H13-1E

PLOG / 0.039 8.92E+18 -2.94 19897 / ! 800 K-2000 K

PLOG / 0.197 6.83E+22 -3.82 23511 / ! 800 K-2000 K

PLOG / 1.000 1.56E+29 -5.39 29211 / ! 800 K-2000 K

PLOG / 10.000 4.15E+37 -7.44 37753 / ! 800 K-2000 K

PLOG / 100.000 1.92E+39 -7.58 42286 / ! 800 K-2000 K

PLOG / 1.0E+5 2.53E+13 0.16 29785 / ! 800 K-2000 K

CH2CHcC6H11+H(+M) = SXC2H4cC6H11(+M) 6.65E+12 0.00 1559.8 ! Refa to C3H6+H(+M) = iC3H7(+M) /2

LOW / 4.35E+42 -7.50 4721.8/

TROE / 1.000 1000.0 645.4 6844.3 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C2H5TXcC6H10=CH2cC6H10+CH3 8.20E+18 -2.83 21257 ! HPL est 2-methyl-2-butyl radical, 2006 Curran, Int. J. Chem. Kinet. 38 (2006) 250-275, fall off from C2H5TXcC6H10=C2H5-2-PXC6H10.

PLOG / 0.039 8.20E+18 -2.83 21257 /

PLOG / 0.197 2.60E+20 -3.03 23458 /

PLOG / 1.000 3.65E+28 -5.11 30284 /

PLOG / 10.000 3.21E+37 -7.30 39149 /

PLOG / 100.000 3.59E+40 -7.83 44643 /

PLOG / 1.0E+5 2.65E+10 1.19 30280 /

C2H5TXcC6H10=C2H5-2-PXC6H10 7.77E+21 -3.78 22330 ! Refa to T1XMCH=P6XC6H10-1E2M

PLOG / 0.039 7.77E+21 -3.78 22330 / ! 800 K-2000 K

PLOG / 0.197 2.46E+23 -3.98 24528 / ! 800 K-2000 K

PLOG / 1.000 3.46E+31 -6.06 31348 / ! 800 K-2000 K

PLOG / 10.000 3.04E+40 -8.25 40204 / ! 800 K-2000 K

PLOG / 100.000 3.40E+43 -8.78 45692 / ! 800 K-2000 K

PLOG / 1.0E+5 2.51E+13 0.24 31344 / ! 800 K-2000 K

C2H5TXcC6H10=CH3CHcC6H10+H 7.35E+21 -4.09 24874 ! EST C2H5TXcC6H10=C2H5-1-cC6H9+H /2

PLOG / 0.039 7.35E+21 -4.09 24874 /

PLOG / 0.197 7.85E+22 -4.12 26671 /

PLOG / 1.000 3.92E+31 -6.33 33844 /

PLOG / 10.000 3.42E+41 -8.76 43572 /

PLOG / 100.000 3.97E+45 -9.52 50174 /

PLOG / 1.0E+5 2.90E+12 0.46 34881 /

C2H5TXcC6H10=C2H5-1-cC6H9+H 1.47E+22 -4.09 24874 ! Refa to T1XMCH=MCH-1E+H

PLOG / 0.039 1.47E+22 -4.09 24874 / ! 800 K-2000 K

PLOG / 0.197 1.57E+23 -4.12 26671 / ! 800 K-2000 K

PLOG / 1.000 7.83E+31 -6.33 33844 / ! 800 K-2000 K

PLOG / 10.000 6.83E+41 -8.76 43572 / ! 800 K-2000 K

PLOG / 100.000 7.93E+45 -9.52 50174 / ! 800 K-2000 K

PLOG / 1.0E+5 5.80E+12 0.46 34881 / ! 800 K-2000 K

C2H5S2XcC6H10= C2H5-3-PXC6H10 1.24E+22 -4.01 22066 ! Refa to S2XMCH=P6XC6H10-1E3M

PLOG / 0.039 1.24E+22 -4.01 22066 / ! 800 K-2000 K

PLOG / 0.197 4.17E+22 -3.93 23430 / ! 800 K-2000 K

PLOG / 1.000 1.01E+28 -5.23 28271 / ! 800 K-2000 K

PLOG / 10.000 2.14E+37 -7.54 37062 / ! 800 K-2000 K

PLOG / 100.000 1.11E+43 -8.81 44209 / ! 800 K-2000 K

PLOG / 1.0E+5 1.59E+13 0.22 31118 / ! 800 K-2000 K

C2H5S2XcC6H10= P8XC8H15-3E 2.99E+22 -4.04 21843 ! Refa to S2XMCH=P7XC7H13-2E

PLOG / 0.039 2.99E+22 -4.04 21843 / ! 800 K-2000 K

PLOG / 0.197 8.66E+22 -3.95 23164 / ! 800 K-2000 K

PLOG / 1.000 1.44E+28 -5.21 27888 / ! 800 K-2000 K

PLOG / 10.000 1.61E+37 -7.45 36452 / ! 800 K-2000 K

PLOG / 100.000 4.39E+42 -8.66 43334 / ! 800 K-2000 K

PLOG / 1.0E+5 2.37E+13 0.19 30429 / ! 800 K-2000 K

C2H5S2XcC6H10=C2H5-1-cC6H9+H 2.06E+20 -3.80 23117 ! Refa to S2XMCH=MCH-1E+H

PLOG / 0.039 2.06E+20 -3.80 23117 / ! 800 K-2000 K

PLOG / 0.197 1.50E+21 -3.78 24651 / ! 800 K-2000 K

PLOG / 1.000 2.14E+27 -5.27 30013 / ! 800 K-2000 K

PLOG / 10.000 8.88E+37 -7.90 39841 / ! 800 K-2000 K

PLOG / 100.000 9.49E+44 -9.50 48246 / ! 800 K-2000 K

PLOG / 1.0E+5 5.69E+11 0.60 34004 / ! 800 K-2000 K

C2H5S2XcC6H10=C2H5-3-cC6H9+H 1.82E+20 -3.68 23447 ! Refa to S2XMCH=MCH-2E+H

PLOG / 0.039 1.82E+20 -3.68 23447 / ! 800 K-2000 K

PLOG / 0.197 1.92E+21 -3.70 25053 / ! 800 K-2000 K

PLOG / 1.000 5.62E+27 -5.27 30610 / ! 800 K-2000 K

PLOG / 10.000 7.34E+38 -8.02 40816 / ! 800 K-2000 K

PLOG / 100.000 2.67E+46 -9.75 49698 / ! 800 K-2000 K

PLOG / 1.0E+5 2.01E+12 0.63 35196 / ! 800 K-2000 K

C2H5S2XcC6H10= cC6H10+C2H5 4.24E+21 -3.89 20767 ! Refa to S2XMCH=cC6H10+CH3, energy barrier reduced 2.1 kcal/mol PLOG / 0.039 4.24E+21 -3.89 20767 / ! 800 K-2000 K

PLOG / 0.197 2.58E+22 -3.86 22260 / ! 800 K-2000 K

PLOG / 1.000 2.27E+28 -5.30 27471 / ! 800 K-2000 K

PLOG / 10.000 4.14E+38 -7.84 36988 / ! 800 K-2000 K

PLOG / 100.000 1.94E+45 -9.36 45005 / ! 800 K-2000 K
PLOG / 1.0E+5 6.35E+13 0.20 31424 / ! 800 K-2000 K
C2H5S3XcC6H10= PXC2H4-4-1C6H11 1.21E+18 -2.84 19903 ! Refa to S3XMCH=P6XC6H1
1E4M
PLOG / 0.039 1.21E+18 -2.84 19903 / ! 800 K-2000 K
PLOG / 0.197 7.98E+21 -3.70 23365 / ! 800 K-2000 K
PLOG / 1.000 2.52E+28 -5.31 28978 / ! 800 K-2000 K
PLOG / 10.000 8.05E+37 -7.66 38033 / ! 800 K-2000 K
PLOG / 100.000 6.13E+42 -8.70 44718 / ! 800 K-2000 K
PLOG / 1.0E+5 1.68E+13 0.21 31241 / ! 800 K-2000 K
C2H5S3XcC6H10 = S6XC8H15-1E 5.23E+18 -2.93 19555 ! Refa to S3XMCH=S6XC7H13-1E
PLOG / 0.039 5.23E+18 -2.93 19555 / ! 800 K-2000 K
PLOG / 0.197 2.06E+22 -3.73 22876 / ! 800 K-2000 K
PLOG / 1.000 3.29E+28 -5.27 28275 / ! 800 K-2000 K
PLOG / 10.000 3.31E+37 -7.49 36918 / ! 800 K-2000 K
PLOG / 100.000 8.80E+41 -8.42 43157 / ! 800 K-2000 K
PLOG / 1.0E+5 2.55E+13 0.17 30061 / ! 800 K-2000 K
C2H5S3XcC6H10=C2H5-4-cC6H9+H 1.19E+16 -2.44 20998 ! Refa to S3XMCH=MCH-3E+H
PLOG / 0.039 1.19E+16 -2.44 20998 / ! 800 K-2000 K
PLOG / 0.197 5.50E+20 -3.50 24928 / ! 800 K-2000 K
PLOG / 1.000 1.93E+28 -5.37 31247 / ! 800 K-2000 K
PLOG / 10.000 3.19E+39 -8.14 41683 / ! 800 K-2000 K
PLOG / 100.000 1.03E+46 -9.58 49952 / ! 800 K-2000 K
PLOG / 1.0E+5 1.87E+12 0.63 34980 / ! 800 K-2000 K
C2H5S3XcC6H10=C2H5-3-cC6H9+H 6.78E+14 -2.23 21396 ! Refa to S3XMCH=MCH-2E+H
PLOG / 0.039 6.78E+14 -2.23 21396 / ! 800 K-2000 K
PLOG / 0.197 8.10E+19 -3.39 25518 / ! 800 K-2000 K
PLOG / 1.000 8.05E+27 -5.38 32106 / ! 800 K-2000 K
PLOG / 10.000 6.73E+39 -8.33 43061 / ! 800 K-2000 K
PLOG / 100.000 1.12E+47 -9.95 51964 / ! 800 K-2000 K
PLOG / 1.0E+5 1.64E+12 0.61 36658 / ! 800 K-2000 K
C2H5S4XcC6H10= PXCH2-5-1C7H13 1.26E+22 -3.85 22627 ! Refa to S4XMCH=P6XC6H10
1E5M
PLOG / 0.039 1.26E+22 -3.85 22627 / ! 800 K-2000 K
PLOG / 0.197 3.57E+26 -4.89 26638 / ! 800 K-2000 K
PLOG / 1.000 2.59E+32 -6.32 32020 / ! 800 K-2000 K
PLOG / 10.000 2.07E+41 -8.51 40814 / ! 800 K-2000 K

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PLOG / 100.000 5.79E+44 -9.15 46530 / ! 800 K-2000 K
PLOG / 1.0E+5 3.87E+13 0.20 31782 / ! 800 K-2000 K
C2H5S4XcC6H10=C2H5-4-cC6H9+H 8.38E+20 -3.63 23771 ! Refa to S4XMCH=MCH-3E+H
PLOG / 0.039 8.38E+20 -3.63 23771 / ! 800 K-2000 K
PLOG / 0.197 8.32E+25 -4.80 28120 / ! 800 K-2000 K
PLOG / 1.000 5.73E+32 -6.47 34206 / ! 800 K-2000 K
PLOG / 10.000 1.37E+43 -9.02 44242 / ! 800 K-2000 K
PLOG / 100.000 7.21E+47 -9.98 51272 / ! 800 K-2000 K
PLOG / 1.0E+5 3.78E+12 0.63 34881 / ! 800 K-2000 K
! Ethylcyclohexane radical reactions
PXC2H4cC6H11 = C2H5S2XcC6H10 4.58E+08 0.90 22900.0 ! 09/SI-WA JetSurF 2.0
PLOG / 0.039 2.29E+07 0.90 22900.0/ ! /20 EST
PLOG / 1.0 4.58E+08 0.90 22900.0/ !
PXC2H4cC6H11 = C2H5S3XcC6H10 4.94E+08 0.78 18644.0 ! 09/SI-WA JetSurF 2.0
PLOG / 0.039 2.47E+07 0.78 18644.0/ ! /20 EST
PLOG / 1.0 4.94E+08 0.78 18644.0/ !
PXC2H4cC6H11 = C2H5S4XcC6H10 7.97E+08 0.78 22740.0 ! 09/SI-WA JetSurF 2.0
PLOG / 0.039 4.00E+07 0.78 22740.0/ ! /20 EST
PLOG / 1.0 7.97E+08 0.78 22740.0/ !
SXC2H4cC6H11 = C2H5S3XcC6H10 4.65E+08 1.02 28687.0 ! 09/SI-WA JetSurF 2.0
PLOG / 0.039 2.33E+07 1.02 28687.0/ ! /20 EST
PLOG / 1.0 4.65E+08 1.02 28687.0/ !
SXC2H4cC6H11 = C2H5S4XcC6H10 1.19E+09 0.92 22700.0 ! 09/SI-WA JetSurF 2.0
PLOG / 0.039 5.95E+07 0.92 22700.0/ ! /20 EST
PLOG / 1.0 1.19E+09 0.92 22700.0/ !
PXC2H4cC6H11(+M) = cC6H11+C2H4(+M) 6.03E+10 0.84 27820.0 ! 08TSAb
LOW / 1.00E-43 18.591 -602.5/
TROE/ -43.32 200.0 28.0 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
CH2CHcC6H11+H(+M)=PXC2H4cC6H11(+M) 1.33E+13 0.00 3260.7 ! Refa to C3H6+H(+M) = nC3H7(+M)
LOW / 6.26E+38 -6.66 7000.0/
TROE/ 1.000 1000.0 1310.0 48097.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
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SXC2H4cC6H11=P8XC8H15-2E 8.92E+18 -2.94 19897 ! Refa to PXCH2cC6H11=P7XC7H1
1E
PLOG / 0.039 8.92E+18 -2.94 19897 / ! 800 K-2000 K
PLOG / 0.197 6.83E+22 -3.82 23511 / ! 800 K-2000 K
PLOG / 1.000 1.56E+29 -5.39 29211 / ! 800 K-2000 K
PLOG / 10.000 4.15E+37 -7.44 37753 / ! 800 K-2000 K
PLOG / 100.000 1.92E+39 -7.58 42286 / ! 800 K-2000 K
PLOG / 1.0E+5 2.53E+13 0.16 29785 / ! 800 K-2000 K
CH2CHcC6H11+H(+M) = SXC2H4cC6H11(+M) 6.65E+12 0.00 1559.8 ! Refa to C3H6+H(+M) = iC3H7(+M) /2
LOW / 4.35E+42 -7.50 4721.8/
TROE / 1.000 1000.0 645.4 6844.3 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C2H5TXcC6H10=CH2cC6H10+CH3 8.20E+18 -2.83 21257 ! HPL est 2-methyl-2-butyl radical, 2006 Curran, Int. J. Chem. Kinet. 38 (2006) 250-275, fall off from C2H5TXcC6H10=C2H5-2-PXC6H10.
PLOG / 0.039 8.20E+18 -2.83 21257 /
PLOG / 0.197 2.60E+20 -3.03 23458 /
PLOG / 1.000 3.65E+28 -5.11 30284 /
PLOG / 10.000 3.21E+37 -7.30 39149 /
PLOG / 100.000 3.59E+40 -7.83 44643 /
PLOG / 1.0E+5 2.65E+10 1.19 30280 /
C2H5TXcC6H10=C2H5-2-PXC6H10 7.77E+21 -3.78 22330 ! Refa to T1XMCH=P6XC6H10-1E2M
PLOG / 0.039 7.77E+21 -3.78 22330 / ! 800 K-2000 K
PLOG / 0.197 2.46E+23 -3.98 24528 / ! 800 K-2000 K
PLOG / 1.000 3.46E+31 -6.06 31348 / ! 800 K-2000 K
PLOG / 10.000 3.04E+40 -8.25 40204 / ! 800 K-2000 K
PLOG / 100.000 3.40E+43 -8.78 45692 / ! 800 K-2000 K
PLOG / 1.0E+5 2.51E+13 0.24 31344 / ! 800 K-2000 K
C2H5TXcC6H10=CH3CHcC6H10+H 7.35E+21 -4.09 24874 ! EST C2H5TXcC6H10=C2H5-1-cC6H9+H /2
PLOG / 0.039 7.35E+21 -4.09 24874 /
PLOG / 0.197 7.85E+22 -4.12 26671 /
PLOG / 1.000 3.92E+31 -6.33 33844 /
PLOG / 10.000 3.42E+41 -8.76 43572 /
PLOG / 100.000 3.97E+45 -9.52 50174 /
PLOG / 1.0E+5 2.90E+12 0.46 34881 /
C2H5TXcC6H10=C2H5-1-cC6H9+H 1.47E+22 -4.09 24874 ! Refa to T1XMCH=MCH-1E+H
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PLOG / 0.039 1.47E+22 -4.09 24874 / ! 800 K-2000 K
PLOG / 0.197 1.57E+23 -4.12 26671 / ! 800 K-2000 K
PLOG / 1.000 7.83E+31 -6.33 33844 / ! 800 K-2000 K
PLOG / 10.000 6.83E+41 -8.76 43572 / ! 800 K-2000 K
PLOG / 100.000 7.93E+45 -9.52 50174 / ! 800 K-2000 K
PLOG / 1.0E+5 5.80E+12 0.46 34881 / ! 800 K-2000 K
C2H5S2XcC6H10= C2H5-3-PXC6H10 1.24E+22 -4.01 22066 ! Refa to S2XMCH=P6XC6H10-1E3M
PLOG / 0.039 1.24E+22 -4.01 22066 / ! 800 K-2000 K
PLOG / 0.197 4.17E+22 -3.93 23430 / ! 800 K-2000 K
PLOG / 1.000 1.01E+28 -5.23 28271 / ! 800 K-2000 K
PLOG / 10.000 2.14E+37 -7.54 37062 / ! 800 K-2000 K
PLOG / 100.000 1.11E+43 -8.81 44209 / ! 800 K-2000 K
PLOG / 1.0E+5 1.59E+13 0.22 31118 / ! 800 K-2000 K
C2H5S2XcC6H10= P8XC8H15-3E 2.99E+22 -4.04 21843 ! Refa to S2XMCH=P7XC7H13-2E
PLOG / 0.039 2.99E+22 -4.04 21843 / ! 800 K-2000 K
PLOG / 0.197 8.66E+22 -3.95 23164 / ! 800 K-2000 K
PLOG / 1.000 1.44E+28 -5.21 27888 / ! 800 K-2000 K
PLOG / 10.000 1.61E+37 -7.45 36452 / ! 800 K-2000 K
PLOG / 100.000 4.39E+42 -8.66 43334 / ! 800 K-2000 K
PLOG / 1.0E+5 2.37E+13 0.19 30429 / ! 800 K-2000 K
C2H5S2XcC6H10=C2H5-1-cC6H9+H 2.06E+20 -3.80 23117 ! Refa to S2XMCH=MCH-1E+H
PLOG / 0.039 2.06E+20 -3.80 23117 / ! 800 K-2000 K
PLOG / 0.197 1.50E+21 -3.78 24651 / ! 800 K-2000 K
PLOG / 1.000 2.14E+27 -5.27 30013 / ! 800 K-2000 K
PLOG / 10.000 8.88E+37 -7.90 39841 / ! 800 K-2000 K
PLOG / 100.000 9.49E+44 -9.50 48246 / ! 800 K-2000 K
PLOG / 1.0E+5 5.69E+11 0.60 34004 / ! 800 K-2000 K
C2H5S2XcC6H10=C2H5-3-cC6H9+H 1.82E+20 -3.68 23447 ! Refa to S2XMCH=MCH-2E+H
PLOG / 0.039 1.82E+20 -3.68 23447 / ! 800 K-2000 K
PLOG / 0.197 1.92E+21 -3.70 25053 / ! 800 K-2000 K
PLOG / 1.000 5.62E+27 -5.27 30610 / ! 800 K-2000 K
PLOG / 10.000 7.34E+38 -8.02 40816 / ! 800 K-2000 K
PLOG / 100.000 2.67E+46 -9.75 49698 / ! 800 K-2000 K
PLOG / 1.0E+5 2.01E+12 0.63 35196 / ! 800 K-2000 K
C2H5S2XcC6H10= cC6H10+C2H5 4.24E+21 -3.89 20767 ! Refa to S2XMCH=cC6H10+CH3, energy barrier reduced 2.1 kcal/mol PLOG / 0.039 4.24E+21 -3.89 20767 / ! 800

K-2000 K
PLOG / 0.197 2.58E+22 -3.86 22260 / ! 800 K-2000 K
PLOG / 1.000 2.27E+28 -5.30 27471 / ! 800 K-2000 K
PLOG / 10.000 4.14E+38 -7.84 36988 / ! 800 K-2000 K
PLOG / 100.000 1.94E+45 -9.36 45005 / ! 800 K-2000 K
PLOG / 1.0E+5 6.35E+13 0.20 31424 / ! 800 K-2000 K
C2H5S3XcC6H10= PXC2H4-4-1C6H11 1.21E+18 -2.84 19903 ! Refa to S3XMCH=P6XC6H1
1E4M
PLOG / 0.039 1.21E+18 -2.84 19903 / ! 800 K-2000 K
PLOG / 0.197 7.98E+21 -3.70 23365 / ! 800 K-2000 K
PLOG / 1.000 2.52E+28 -5.31 28978 / ! 800 K-2000 K
PLOG / 10.000 8.05E+37 -7.66 38033 / ! 800 K-2000 K
PLOG / 100.000 6.13E+42 -8.70 44718 / ! 800 K-2000 K
PLOG / 1.0E+5 1.68E+13 0.21 31241 / ! 800 K-2000 K
C2H5S3XcC6H10 = S6XC8H15-1E 5.23E+18 -2.93 19555 ! Refa to S3XMCH=S6XC7H13-
1E
PLOG / 0.039 5.23E+18 -2.93 19555 / ! 800 K-2000 K
PLOG / 0.197 2.06E+22 -3.73 22876 / ! 800 K-2000 K
PLOG / 1.000 3.29E+28 -5.27 28275 / ! 800 K-2000 K
PLOG / 10.000 3.31E+37 -7.49 36918 / ! 800 K-2000 K
PLOG / 100.000 8.80E+41 -8.42 43157 / ! 800 K-2000 K
PLOG / 1.0E+5 2.55E+13 0.17 30061 / ! 800 K-2000 K
C2H5S3XcC6H10=C2H5-4-cC6H9+H 1.19E+16 -2.44 20998 ! Refa to S3XMCH=MCH-
3E+H
PLOG / 0.039 1.19E+16 -2.44 20998 / ! 800 K-2000 K
PLOG / 0.197 5.50E+20 -3.50 24928 / ! 800 K-2000 K
PLOG / 1.000 1.93E+28 -5.37 31247 / ! 800 K-2000 K
PLOG / 10.000 3.19E+39 -8.14 41683 / ! 800 K-2000 K
PLOG / 100.000 1.03E+46 -9.58 49952 / ! 800 K-2000 K
PLOG / 1.0E+5 1.87E+12 0.63 34980 / ! 800 K-2000 K
C2H5S3XcC6H10=C2H5-3-cC6H9+H 6.78E+14 -2.23 21396 ! Refa to S3XMCH=MCH-
2E+H
PLOG / 0.039 6.78E+14 -2.23 21396 / ! 800 K-2000 K
PLOG / 0.197 8.10E+19 -3.39 25518 / ! 800 K-2000 K
PLOG / 1.000 8.05E+27 -5.38 32106 / ! 800 K-2000 K
PLOG / 10.000 6.73E+39 -8.33 43061 / ! 800 K-2000 K
PLOG / 100.000 1.12E+47 -9.95 51964 / ! 800 K-2000 K
PLOG / 1.0E+5 1.64E+12 0.61 36658 / ! 800 K-2000 K
C2H5S4XcC6H10= PXCH2-5-1C7H13 1.26E+22 -3.85 22627 ! Refa to S4XMCH=P6XC6H10
1E5M

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PLOG / 0.039 1.26E+22 -3.85 22627 / ! 800 K-2000 K
PLOG / 0.197 3.57E+26 -4.89 26638 / ! 800 K-2000 K
PLOG / 1.000 2.59E+32 -6.32 32020 / ! 800 K-2000 K
PLOG / 10.000 2.07E+41 -8.51 40814 / ! 800 K-2000 K
PLOG / 100.000 5.79E+44 -9.15 46530 / ! 800 K-2000 K
PLOG / 1.0E+5 3.87E+13 0.20 31782 / ! 800 K-2000 K
C2H5S4XcC6H10=C2H5-4-cC6H9+H 8.38E+20 -3.63 23771 ! Refa to S4XMCH=MCH-3E+H
PLOG / 0.039 8.38E+20 -3.63 23771 / ! 800 K-2000 K
PLOG / 0.197 8.32E+25 -4.80 28120 / ! 800 K-2000 K
PLOG / 1.000 5.73E+32 -6.47 34206 / ! 800 K-2000 K
PLOG / 10.000 1.37E+43 -9.02 44242 / ! 800 K-2000 K
PLOG / 100.000 7.21E+47 -9.98 51272 / ! 800 K-2000 K
PLOG / 1.0E+5 3.78E+12 0.63 34881 / ! 800 K-2000 K
! Ethylcyclohexane radical reactions
PXC2H4cC6H11 = C2H5S2XcC6H10 4.58E+08 0.90 22900.0 ! 09/SI-WA JetSurF 2.0
PLOG / 0.039 2.29E+07 0.90 22900.0/ ! /20 EST
PLOG / 1.0 4.58E+08 0.90 22900.0/ !
PXC2H4cC6H11 = C2H5S3XcC6H10 4.94E+08 0.78 18644.0 ! 09/SI-WA JetSurF 2.0
PLOG / 0.039 2.47E+07 0.78 18644.0/ ! /20 EST
PLOG / 1.0 4.94E+08 0.78 18644.0/ !
PXC2H4cC6H11 = C2H5S4XcC6H10 7.97E+08 0.78 22740.0 ! 09/SI-WA JetSurF 2.0
PLOG / 0.039 4.00E+07 0.78 22740.0/ ! /20 EST
PLOG / 1.0 7.97E+08 0.78 22740.0/ !
SXC2H4cC6H11 = C2H5S3XcC6H10 4.65E+08 1.02 28687.0 ! 09/SI-WA JetSurF 2.0
PLOG / 0.039 2.33E+07 1.02 28687.0/ ! /20 EST
PLOG / 1.0 4.65E+08 1.02 28687.0/ !
SXC2H4cC6H11 = C2H5S4XcC6H10 1.19E+09 0.92 22700.0 ! 09/SI-WA JetSurF 2.0
PLOG / 0.039 5.95E+07 0.92 22700.0/ ! /20 EST
PLOG / 1.0 1.19E+09 0.92 22700.0/ !
PXC2H4cC6H11(+M) = cC6H11+C2H4(+M) 6.03E+10 0.84 27820.0 ! 08TSAb
LOW / 1.00E-43 18.591 -602.5/
TROE/ -43.32 200.0 28.0 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
```

CH2CHcC6H11+H(+M)=PXC2H4cC6H11(+M) 1.33E+13 0.00 3260.7 ! Refa to C3H6+H(+M) = nC3H7(+M)

LOW / 6.26E+38 -6.66 7000.0/

TROE/ 1.000 1000.0 1310.0 48097.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

SXC2H4cC6H11=P8XC8H15-2E 8.92E+18 -2.94 19897 ! Refa to PXCH2cC6H11=P7XC7H1
1E

PLOG / 0.039 8.92E+18 -2.94 19897 / ! 800 K-2000 K

PLOG / 0.197 6.83E+22 -3.82 23511 / ! 800 K-2000 K

PLOG / 1.000 1.56E+29 -5.39 29211 / ! 800 K-2000 K

PLOG / 10.000 4.15E+37 -7.44 37753 / ! 800 K-2000 K

PLOG / 100.000 1.92E+39 -7.58 42286 / ! 800 K-2000 K

PLOG / 1.0E+5 2.53E+13 0.16 29785 / ! 800 K-2000 K

CH2CHcC6H11+H(+M) = SXC2H4cC6H11(+M) 6.65E+12 0.00 1559.8 ! Refa to C3H6+H(+M) = iC3H7(+M) /2

LOW / 4.35E+42 -7.50 4721.8/

TROE / 1.000 1000.0 645.4 6844.3 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C2H5TXcC6H10=CH2cC6H10+CH3 8.20E+18 -2.83 21257 ! HPL est 2-methyl-2-butyl radical, 2006 Curran, Int. J. Chem. Kinet. 38 (2006) 250-275, fall off from C2H5TXcC6H10=C2H5-2-PXC6H10.

PLOG / 0.039 8.20E+18 -2.83 21257 /

PLOG / 0.197 2.60E+20 -3.03 23458 /

PLOG / 1.000 3.65E+28 -5.11 30284 /

PLOG / 10.000 3.21E+37 -7.30 39149 /

PLOG / 100.000 3.59E+40 -7.83 44643 /

PLOG / 1.0E+5 2.65E+10 1.19 30280 /

C2H5TXcC6H10=C2H5-2-PXC6H10 7.77E+21 -3.78 22330 ! Refa to T1XMCH=P6XC6H10-
1E2M

PLOG / 0.039 7.77E+21 -3.78 22330 / ! 800 K-2000 K

PLOG / 0.197 2.46E+23 -3.98 24528 / ! 800 K-2000 K

PLOG / 1.000 3.46E+31 -6.06 31348 / ! 800 K-2000 K

PLOG / 10.000 3.04E+40 -8.25 40204 / ! 800 K-2000 K

PLOG / 100.000 3.40E+43 -8.78 45692 / ! 800 K-2000 K

PLOG / 1.0E+5 2.51E+13 0.24 31344 / ! 800 K-2000 K

C2H5TXcC6H10=CH3CHcC6H10+H 7.35E+21 -4.09 24874 ! EST C2H5TXcC6H10=C2H5-
1-cC6H9+H /2

PLOG / 0.039 7.35E+21 -4.09 24874 /

PLOG / 0.197 7.85E+22 -4.12 26671 /

PLOG / 1.000 3.92E+31 -6.33 33844 /

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PLOG / 10.000 3.42E+41 -8.76 43572 /
PLOG / 100.000 3.97E+45 -9.52 50174 /
PLOG / 1.0E+5 2.90E+12 0.46 34881 /
C2H5TXcC6H10=C2H5-1-cC6H9+H 1.47E+22 -4.09 24874 ! Refa to T1XMCH=MCH-1E+H
PLOG / 0.039 1.47E+22 -4.09 24874 / ! 800 K-2000 K
PLOG / 0.197 1.57E+23 -4.12 26671 / ! 800 K-2000 K
PLOG / 1.000 7.83E+31 -6.33 33844 / ! 800 K-2000 K
PLOG / 10.000 6.83E+41 -8.76 43572 / ! 800 K-2000 K
PLOG / 100.000 7.93E+45 -9.52 50174 / ! 800 K-2000 K
PLOG / 1.0E+5 5.80E+12 0.46 34881 / ! 800 K-2000 K
C2H5S2XcC6H10= C2H5-3-PXC6H10 1.24E+22 -4.01 22066 ! Refa to S2XMCH=P6XC6H10-1E3M
PLOG / 0.039 1.24E+22 -4.01 22066 / ! 800 K-2000 K
PLOG / 0.197 4.17E+22 -3.93 23430 / ! 800 K-2000 K
PLOG / 1.000 1.01E+28 -5.23 28271 / ! 800 K-2000 K
PLOG / 10.000 2.14E+37 -7.54 37062 / ! 800 K-2000 K
PLOG / 100.000 1.11E+43 -8.81 44209 / ! 800 K-2000 K
PLOG / 1.0E+5 1.59E+13 0.22 31118 / ! 800 K-2000 K
C2H5S2XcC6H10= P8XC8H15-3E 2.99E+22 -4.04 21843 ! Refa to S2XMCH=P7XC7H13-2E
PLOG / 0.039 2.99E+22 -4.04 21843 / ! 800 K-2000 K
PLOG / 0.197 8.66E+22 -3.95 23164 / ! 800 K-2000 K
PLOG / 1.000 1.44E+28 -5.21 27888 / ! 800 K-2000 K
PLOG / 10.000 1.61E+37 -7.45 36452 / ! 800 K-2000 K
PLOG / 100.000 4.39E+42 -8.66 43334 / ! 800 K-2000 K
PLOG / 1.0E+5 2.37E+13 0.19 30429 / ! 800 K-2000 K
C2H5S2XcC6H10=C2H5-1-cC6H9+H 2.06E+20 -3.80 23117 ! Refa to S2XMCH=MCH-1E+H
PLOG / 0.039 2.06E+20 -3.80 23117 / ! 800 K-2000 K
PLOG / 0.197 1.50E+21 -3.78 24651 / ! 800 K-2000 K
PLOG / 1.000 2.14E+27 -5.27 30013 / ! 800 K-2000 K
PLOG / 10.000 8.88E+37 -7.90 39841 / ! 800 K-2000 K
PLOG / 100.000 9.49E+44 -9.50 48246 / ! 800 K-2000 K
PLOG / 1.0E+5 5.69E+11 0.60 34004 / ! 800 K-2000 K
C2H5S2XcC6H10=C2H5-3-cC6H9+H 1.82E+20 -3.68 23447 ! Refa to S2XMCH=MCH-2E+H
PLOG / 0.039 1.82E+20 -3.68 23447 / ! 800 K-2000 K
PLOG / 0.197 1.92E+21 -3.70 25053 / ! 800 K-2000 K
PLOG / 1.000 5.62E+27 -5.27 30610 / ! 800 K-2000 K
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PLOG / 10.000 7.34E+38 -8.02 40816 / ! 800 K-2000 K

PLOG / 100.000 2.67E+46 -9.75 49698 / ! 800 K-2000 K

PLOG / 1.0E+5 2.01E+12 0.63 35196 / ! 800 K-2000 K

C2H5S2XcC6H10= cC6H10+C2H5 4.24E+21 -3.89 20767 ! Refa to S2XMCH=cC6H10+CH3
energy barrier reduced 2.1 kcal/mol PLOG / 0.039 4.24E+21 -3.89 20767 / ! 800 K-2000 K

PLOG / 0.197 2.58E+22 -3.86 22260 / ! 800 K-2000 K

PLOG / 1.000 2.27E+28 -5.30 27471 / ! 800 K-2000 K

PLOG / 10.000 4.14E+38 -7.84 36988 / ! 800 K-2000 K

PLOG / 100.000 1.94E+45 -9.36 45005 / ! 800 K-2000 K

PLOG / 1.0E+5 6.35E+13 0.20 31424 / ! 800 K-2000 K

C2H5S3XcC6H10= PXC2H4-4-1C6H11 1.21E+18 -2.84 19903 ! Refa to S3XMCH=P6XC6H1
1E4M

PLOG / 0.039 1.21E+18 -2.84 19903 / ! 800 K-2000 K

PLOG / 0.197 7.98E+21 -3.70 23365 / ! 800 K-2000 K

PLOG / 1.000 2.52E+28 -5.31 28978 / ! 800 K-2000 K

PLOG / 10.000 8.05E+37 -7.66 38033 / ! 800 K-2000 K

PLOG / 100.000 6.13E+42 -8.70 44718 / ! 800 K-2000 K

PLOG / 1.0E+5 1.68E+13 0.21 31241 / ! 800 K-2000 K

C2H5S3XcC6H10 = S6XC8H15-1E 5.23E+18 -2.93 19555 ! Refa to S3XMCH=S6XC7H13-1E

PLOG / 0.039 5.23E+18 -2.93 19555 / ! 800 K-2000 K

PLOG / 0.197 2.06E+22 -3.73 22876 / ! 800 K-2000 K

PLOG / 1.000 3.29E+28 -5.27 28275 / ! 800 K-2000 K

PLOG / 10.000 3.31E+37 -7.49 36918 / ! 800 K-2000 K

PLOG / 100.000 8.80E+41 -8.42 43157 / ! 800 K-2000 K

PLOG / 1.0E+5 2.55E+13 0.17 30061 / ! 800 K-2000 K

C2H5S3XcC6H10=C2H5-4-cC6H9+H 1.19E+16 -2.44 20998 ! Refa to S3XMCH=MCH-3E+H

PLOG / 0.039 1.19E+16 -2.44 20998 / ! 800 K-2000 K

PLOG / 0.197 5.50E+20 -3.50 24928 / ! 800 K-2000 K

PLOG / 1.000 1.93E+28 -5.37 31247 / ! 800 K-2000 K

PLOG / 10.000 3.19E+39 -8.14 41683 / ! 800 K-2000 K

PLOG / 100.000 1.03E+46 -9.58 49952 / ! 800 K-2000 K

PLOG / 1.0E+5 1.87E+12 0.63 34980 / ! 800 K-2000 K

C2H5S3XcC6H10=C2H5-3-cC6H9+H 6.78E+14 -2.23 21396 ! Refa to S3XMCH=MCH-2E+H

PLOG / 0.039 6.78E+14 -2.23 21396 / ! 800 K-2000 K

PLOG / 0.197 8.10E+19 -3.39 25518 / ! 800 K-2000 K

PLOG / 1.000 8.05E+27 -5.38 32106 / ! 800 K-2000 K

PLOG / 10.000 6.73E+39 -8.33 43061 / ! 800 K-2000 K

PLOG / 100.000 1.12E+47 -9.95 51964 / ! 800 K-2000 K

PLOG / 1.0E+5 1.64E+12 0.61 36658 / ! 800 K-2000 K

C2H5S4XcC6H10= PXCH2-5-1C7H13 1.26E+22 -3.85 22627 ! Refa to S4XMCH=P6XC6H10-1E5M

PLOG / 0.039 1.26E+22 -3.85 22627 / ! 800 K-2000 K

PLOG / 0.197 3.57E+26 -4.89 26638 / ! 800 K-2000 K

PLOG / 1.000 2.59E+32 -6.32 32020 / ! 800 K-2000 K

PLOG / 10.000 2.07E+41 -8.51 40814 / ! 800 K-2000 K

PLOG / 100.000 5.79E+44 -9.15 46530 / ! 800 K-2000 K

PLOG / 1.0E+5 3.87E+13 0.20 31782 / ! 800 K-2000 K

C2H5S4XcC6H10=C2H5-4-cC6H9+H 8.38E+20 -3.63 23771 ! Refa to S4XMCH=MCH-3E+H

PLOG / 0.039 8.38E+20 -3.63 23771 / ! 800 K-2000 K

PLOG / 0.197 8.32E+25 -4.80 28120 / ! 800 K-2000 K

PLOG / 1.000 5.73E+32 -6.47 34206 / ! 800 K-2000 K

PLOG / 10.000 1.37E+43 -9.02 44242 / ! 800 K-2000 K

PLOG / 100.000 7.21E+47 -9.98 51272 / ! 800 K-2000 K

PLOG / 1.0E+5 3.78E+12 0.63 34881 / ! 800 K-2000 K

! Ethylcyclohexane reactions

! H abstraction of Ethylcyclohexane

C2H5cC6H11+H = PXC2H4cC6H11+H2 6.66E+06 2.13 8894.8 ! Refer to MCH+H = PXCH2cC6H11+H2

C2H5cC6H11+H = SXC2H4cC6H11+H2 2.55E+05 2.53 4479.0 ! 10LV JetSurF 2.0

C2H5cC6H11+H = C2H5TXcC6H10+H2 4.53E+06 2.11 4098.6 ! Refer to MCH+H = T1XMCH+H2

C2H5cC6H11+H = C2H5S2XcC6H10+H2 2.08E+07 2.10 6474.4 ! Refer to MCH+H = S2XMCH+H2

C2H5cC6H11+H = C2H5S3XcC6H10+H2 2.07E+07 2.12 6441.2 ! Refer to MCH+H = S3XMCH+H2

C2H5cC6H11+H = C2H5S4XcC6H10+H2 1.16E+07 2.11 6339.1 ! Refer to MCH+H = S4XMCH+H2

C2H5cC6H11+CH3 = SXC2H4cC6H11+CH4 7.13E+01 3.25 13556.0 ! 10LV JetSurF 2.0

C2H5cC6H11+CH3 = PXC2H4cC6H11+CH4 3.75E+01 3.27 13516.0 ! Refer to MCH+CH3 = PXCH2cC6H11+CH4

C2H5cC6H11+CH3 = C2H5TXcC6H10+CH4 1.91E+01 3.27 9022.0 ! Refer to MCH+CH3 = T1XMCH+CH4

C2H5cC6H11+CH3 = C2H5S2XcC6H10+CH4 6.68E+01 3.21 11418.0 ! Refer to MCH+CH3 = S2XMCH+CH4

C2H5cC6H11+CH3 = C2H5S3XcC6H10+CH4 7.18E+01 3.26 11303.0 ! Refer to MCH+CH3 = S3XMCH+CH4

C2H5cC6H11+CH3 = C2H5S4XcC6H10+CH4 1.82E+01 3.36 10931.0 ! Refer to MCH+CH3 = S4XMCH+CH4

! isomerization and decomposition of ethylcyclohexane

C2H5cC6H11 = cC6H11+C2H5 1.00 0.00 0.00 ! Refa to MCH = cC6H11+CH3

PLOG / 0.01 1.85E+105 -26.15 129214 /

PLOG / 0.0395 1.19E+92 -22.23 122595 /

PLOG / 0.197 1.50E+80 -18.67 116938 /

PLOG / 0.395 8.65E+63 -13.89 108211 /

PLOG / 1 5.93E+64 -14.15 108486 /

PLOG / 10 3.59E+45 -8.56 97430 /

PLOG / 100 1.66E+33 -4.99 90100 /

PLOG / 1.0E+5 1.10E+27 -3.20 86385 /

C2H5cC6H11(+M) = PXCH2cC6H11+CH3(+M) 6.5E+36 -5.84 9.74E+04 ! Refa to C3H8=C2H5+CH3 /2 Matthew A. Oehlschlaeger, PCI 30 1119-1127

LOW / 2.82E+74 -15.74 9.87E+04/

TROE / 0.31 50 3000 9000 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

! aromatics mechsnism from Yuan et al., Combustion and Flame 162, 3-21; 22-40.

!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!! Submechanism of Toluene !!

!—————————————— Unimolecular dissociation reactions ——————————————————————————————————— A1CH3(+M) = A1CH2+H(+M) 2.78E+15 0.17 9.1168E+04 ! S.J. Klippenstein 2007 PCI

LOW/1.00E+98 -22.855 9.9882E+04/

TROE/6.547194E-02 1.511253E+01 9.999996E+09 7.596123E+07/

A1CH3(+M) = A1-+CH3(+M) 1.95E+27 -3.16 1.07447E+05 ! S.J. Klippenstein 2007 PCI

LOW/1.00E+98 -22.966 1.2208E+05/

TROE/7.054562E-01 9.999989E+09 4.599180E+02 8.213938E+09/

C6H4CH3+H(+M)=A1CH3(+M) 1.00E+14 0.0 0.0 !Refer to A1-+H(+M)=A1(+M) 1997 Wang & Frenklach

LOW / 6.6E+75 -16.30 7000.0/

TROE/ 1.0 0.1 584.9 6113.0/

H2/2.0/ CH4/2.0/ C2H6/3.0/

!—————————————— H-Abstraction reactions————————————————————————————————————- A1CH3+H=A1CH2+H2 6.47E+00 3.98 3384.0

!2006 Oehlschlaeger et al. J.Phys.Chem A 110,2006 9867-9873

A1CH3+H=C6H4CH3+H2 3.910e+08 1.800 16352.77 !Narayanaswamy et al. Combustion and Flame 157 (2010) 1879-1898

A1CH3+H=A1+CH3 3.90E+08 1.25 2371 !Vasu, Davidson and Hanson 2010, the data is fitted base on the recommendation of Baulch and Ellis

! lead to too much toluene formation !!!C3H3+C4H6=A1CH3+H 3.27E+6 1.28 -4611.0 !Laskin et al. IJCK 32 589-614 2000 6.53E+5 *5 TO interpret the A1CH3 formation in C5H6 flow reactor oxidation

!est in this work C3H3+C4H6=A1CH3+H 3.75E+5 1.28 -4611.0 !Laskin et al. IJCK 32 589-614 2000 /2

A1CH3+CH3=A1CH2+CH4 4.220e+14 0.000 22256.21 !Narayanaswamy et al. Combustion and Flame 157 (2010) 1879-1898

A1CH3+CH3=C6H4CH3+CH4 1.790E-02 4.460 13637.67 !Narayanaswamy et al. Combustion and Flame 157 (2010) 1879-1898

A1CH3+C2H3=A1CH2+C2H4 3.98E+12 0.0 8000.0 !1995 Zhang & Mckinnon

A1CH3+C3H3=A1CH2+pC3H4 1.6E+12 0.0 15100.0 !Bounaceur et al. 2005 Int J Chem Kinet 37: 25-49

A1CH3+C5H5=A1CH2+C5H6 3.2E+12 0.0 17100.0 !Bounaceur et al. 2005 Int J Chem Kinet 37: 25-49 1.6E+12

A1CH3+A1-=A1CH2+A1 2.68e-01 3.95 877.06 !W. K. Metcalfe et al. Energy & Fuels 25 (2011) 4915-4936

A1CH3+aC3H5=A1CH2+C3H6 1.6E+12 0.0 15100.0 !Bounaceur et al. 2005 Int J Chem Kinet 37: 25-49

A1CH3+iC4H5=A1CH2+C4H6 1.6E+12 0.0 15100.0 !Bounaceur et al. 2005 Int J Chem Kinet 37: 25-49

A1CH3+nC4H5=A1CH2+C4H6 1.6E+12 0.0 15100.0 !Bounaceur et al. 2005 Int J Chem Kinet 37: 25-49

A1CH3+C6H4CH3=A1CH2+A1CH3 7.9E+13 0.0 12000.0 !Bounaceur et al. 2005 Int J Chem Kinet 37: 25-49

nC4H3+pC3H4=¿C6H4CH3 2.40E+10 0.0 0.0 !C. Saggese et al. Combustion and Flame 160 (2013) 1168-1190

C6H4CH3=>nC4H3+pC3H4 4.50E+13 0.0 72500.0 !C. Saggese et al. Combustion and Flame 160 (2013) 1168-1190 ! Decomposition of benzyl(A1CH2), fulvenallene(C7H6) and fulvenallenyl(C7H5)

A1CH2=>C7H6+H 4.47E+129 -32.57 162410.0 !M. Derudi, D. Polino, C. Cavallotti, PCCP, 13 (2011) 21308-21318

PLOG / 0.013 4.47E+129 -32.57 162410.0/

PLOG / 0.130 1.29E+123 -30.34 163830.0/

PLOG / 1.000 2.95E+97 -22.95 148280.0/ !close to the experimental measured results of Ronald k. hanson at 1.5 bar

PLOG/ 1.500 8.20E+14 0.00E+00 8.07E+04/

PLOG / 10.000 1.26E+39 -6.76 99710.0/

PLOG / 50.000 1.44E+13 0.453 76300/ !HPL

C7H6+H=>A1CH2 8.80E+8 1.2 -2020 !C. Cavallotti, M. Derudi, R. Rota, PCI 32 (2009) 115-121.

A1CH2=o-C6H4+CH3 2.04E+135 -34.08 169130 !M. Derudi, D. Polino, C. Cavallotti, PCCP, 13 (2011) 21308-21318

PLOG/ 0.013 2.04E+135 -34.08 169130/

PLOG/ 0.130 6.46E+112 -27.50 155360/

PLOG/ 1.00 5.50E+89 -20.82 141680/

PLOG/ 10.00 5.13E+55 -11.23 116580/

A1CH2+H=A1-+CH3 4.50E+58 -11.9 51860 !S. J. Klippenstein, L. B. Harding, Y. Georgievskii, PC31 (2007) 221-229.

PLOG/ 0.0395 4.50E+58 -11.9 51860/

PLOG/ 0.132 2.03E+64 -13.37 59520/

PLOG/ 1.000 5.83E+67 -14.15 68330/

PLOG/ 10.00 8.85E+68 -14.23 78410/

C7H6=cC5H4+C2H2 1.26E+130 -32.19 173970.0 !D. Polino, C. Cavallotti, JPC A 115 (2011) 10281-10289.

PLOG / 0.100 2.34E+135 -33.58 179460/

PLOG / 1.000 3.02E+124 -30.18 176460/

PLOG / 10.000 4.27E+129 -31.11 191020/

C7H6=C7H5+H 1.02E+116 -28.46 157860.0 !D. Polino, C. Cavallotti, JPC A 115 (2011) 10281-10289.

PLOG / 0.100 1.02E+116 -28.46 157860.0/

PLOG / 1.000 4.90E+66 -14.64 119550.0/

PLOG / 10.000 1.17E+27 -3.54 89150.0/

C5H5+C2H2=>C7H6+H 1.29E+21 -2.38 32400 !G. da Silva, J. A. Cole, J. W. Bozzelli, J. Phys. Chem. A 114 (2010) 2275-2283.

PLOG/ 0.0001 1.29E+21 -2.38 32400/

PLOG/ 0.001 3.37E+12 0.22 31060/

PLOG/ 0.01 7.07E+01 3.42 28740/

PLOG/ 0.1 1.58E-01 4.18 29670/

PLOG/ 1.0 6.96E-05 5.17 30930/

PLOG/ 10.0 2.37E-06 5.60 33540/

PLOG/ 100 1.15E-44 17.07 22460/

PLOG/ 1000 8.31E-37 14.56 29740/

C7H6+H=>C5H5+C2H2 6.81E+24 -3.04 14950 !G. da Silva, J. A. Cole, J. W. Bozzelli, J. Phys. Chem. A 114 (2010) 2275-2283.

PLOG/ 0.0001 6.81E+24 -3.04 14950/

PLOG/ 0.001 6.87E+16 -0.62 13700/

PLOG/ 0.01 5.39E+06 2.41 11550/

PLOG/ 0.1 3.65E+01 3.93 11460/

PLOG/ 1.0 1.22E-06 6.15 11040/

PLOG/ 10.0 2.65E-15 8.75 10810/

PLOG/ 100 8.55E-21 10.35 12590/

PLOG/ 1000 2.05E-30 13.09 13020/

C7H6+H=C7H5+H2 1.90E+08 1.847 4965.0 !G. da Silva, J. W. Bozzelli, J. Phys. Chem. A 113 (2009) 12045-12048.

C7H6+CH3=C7H5+CH4 1.87E+04 2.724 6008.0 !G. da Silva, J. W. Bozzelli, J. Phys. Chem. A 113 (2009) 12045-12048.

C7H5=C4H2+C3H3 8.71E+92 -23.08 117070.0 !M. Derudi, D. Polino, C. Cavallotti, PCCP, 13 (2011) 21308-21318

PLOG / 0.013 8.71E+92 -23.08 117070.0/

PLOG / 0.130 1.82E+102 -25.22 130330.0/

PLOG / 1.000 8.51E+82 -19.18 125340.0/

PLOG / 10.000 2.40E+56 -11.65 106750.0/

nC4H3+C3H3=C7H6 1.00E+13 0.00 0.0 !Y. Sakai et al. PCI32 (2009) 411-418

C7H5=C5H3+C2H2 3.16E+83 -20.81 109410.0 !M. Derudi, D. Polino, C. Cavallotti, PCCP, 13 (2011) 21308-21318

PLOG / 0.013 3.16E+83 -20.81 109410.0/

PLOG / 0.130 7.59E+102 -25.66 132390.0/

PLOG / 1.000 2.82E+90 -21.38 135620.0/

PLOG / 10.000 4.37E+90 -21.04 143990.0/

C6H4CH3=A1CH2 3.09E+73 -18.22 69670 !Enoch Dames & Hai Wang 2013 PCI34

PLOG/ 0.1 3.09E+73 -18.22 69670/

PLOG/ 1.0 2.91E+59 -13.86 64518/

PLOG/ 10.0 6.76E+40 -8.54 54069/

PLOG/ 50.0 3.66E+26 -3.98 49795/

C6H4CH3+H=A1CH2+H 1.0E+13 0.0 0.0 !Bounaceur et al 2005

C6H4CH3=o-C6H4+CH3 6.11E+45 -8.857 94350.6 !1997 Madden et al. RRKM A1-=o-C6H4+H

PLOG / 0.500 6.11E+45 -8.857 94350.6/

PLOG / 1.000 8.00E+41 -7.72 92300.3/

PLOG / 10.000 1.66E+30 -4.318 85756.9/

A1CH2=C5H5+C2H2 4.08E+134 -34.08 169130 !EST this work 5 times slower than the reaction A1CH2=o-C6H4+ch3

PLOG/ 0.013 4.08E+134 -34.08 169130/

PLOG/ 0.130 1.29E+112 -27.50 155360/

PLOG/ 1.00 1.10E+89 -20.82 141680/

PLOG/ 10.00 1.03E+55 -11.23 116580/

PLOG/ 50.000 1.44E+13 0.453 76300/

!************************************ Reactions of benzene(A1) and fulvene ** A1-+H(+M)=A1(+M) 1.00E+14 0.0 0.0 !1997 Wang&Frenklach RRKM

LOW / 6.6E+75 -16.30 7000.0/

TROE/ 1.0 0.1 584.9 6113.0/

H2/2.0/ CH4/2.0/ C2H6/3.0/

!——- A1+H=A1-+H2 2.50E+14 0.0 16000.0 !Emdee et al.J. Phys. Chem. 1992, 96, 2151-2161

A1-+CH4=A1+CH3 3.89E-03 4.6 5256.0 !1999 Tokmakov et al.

A1-+C2H6=A1+C2H5 2.10E+11 0.0 4443.0 !2001 Park et al.

C5H6+A1-=C5H5+A1 3.10E+11 0.0 5500.0 !2001 Bacskay&Mackie

nC4H3+C2H3=A1 2.87E+14 0.0 817.0 !1988 Duran et al. Fit data in 2005 Sivaramakrishnan et al.

C3H3+aC3H5=fulvene+2H 3.26E+29 -5.4 3390.0 !Miller&Klippenstein 2003.

aC3H4+C3H2=A1 7.40E+12 -0.7 920.0 !2002 D'Anna et al.

pC3H4+C3H2=A1 1.40E+13 -0.8 1030.0 !2002 D'Anna et al.

aC3H4+C3H3=A1+H 2.20E+11 0.0 2000.0 !2002 D'Anna et al.

C4H4+C2H3=A1+H 1.90E+12 0.0 2510.0 !1997 Lindstedt&Skevis

pC3H4+C3H3=A1+H 2.20E+11 0.0 2000.0 !1987 Wu&Kern

C4H4+C2H2=A1 4.47E+11 0.0 30010.0 !1986 Chanmugathas&Heicklen

C2H2+nC4H5=H+A1 1.37E16 -1.00 8896 !Miller&Klippenstein 2003

PLOG /0.01 1.37E16 -1.00 8896./

PLOG /0.025 2.94E16 -1.09 9259./

PLOG /0.1 1.37E16 -1.00 8898./

PLOG /1. 1.385E16 -1.00 8900./

PLOG /10. 1.69E16 -1.03 8967./

PLOG /100. 1.65E16 -1.01 9480./

C2H2+nC4H5=H+fulvene 1.52E15 -0.76 8767 !Miller&Klippenstein 2003

PLOG /0.01 1.52E15 -0.76 8767./

PLOG /0.025 1.52E15 -0.76 8767./

PLOG /0.1 1.52E15 -0.76 8769./

PLOG /1. 4.63E15 -0.89 9142./

PLOG /10. 1.74E19 -1.86 12383./

PLOG /100. 1.23E20 -2.00 16152./ !Miller&Klippenstein 2003

C2H2+iC4H5=H+A1 1.47E+23 -3.28 24907 !Miller&Klippenstein 2003

PLOG /0.01 1.47E+23 -3.28 24907./

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PLOG /0.025 1.47E+23 -3.28 24907./
PLOG /0.1 1.47E+23 -3.28 24907./
PLOG /1. 1.67E+23 -3.30 24959./
PLOG /10. 8.25E+24 -3.76 24562./
PLOG /100. 5.37E+32 -5.84 35023./
C2H2+iC4H5=H+fulvene 6.50E+24 -3.44 20319. !Miller&Klippenstein 2003
PLOG /0.01 6.50E+24 -3.44 20319./
PLOG /0.025 1.01E+34 -5.94 28786./
PLOG /0.1 6.50E+24 -3.44 20319./
PLOG /1. 6.80E+24 -3.45 20337./
PLOG /10. 9.70E+25 -3.76 21326./
PLOG /100. 5.22E+41 -7.94 39597./
nC4H5+C2H3=A1+H2 1.84E-13 7.1 -3611.0 !1989 Westmoreland et al.
C3H3+C3H3=fulvene 6.3069E+76 -19.07 31542. !Miller&Klippenstein 2003
PLOG /0.03947 6.3069E+76 -19.07 31542./
PLOG /1. 1.3798E+66 -15.66 28260./
PLOG /10. 1.2584E+56 -12.61 23515./
C3H3+C3H3=A1 1.8189E+74 -18.14 31896. !Miller&Klippenstein 2003
PLOG /0.03947 1.8189E+74 -18.14 31896./
PLOG /1. 3.1609E+55 -12.55 22264./
PLOG /10. 3.8888E+50 -11.01 20320./
fulvene=A1 5.62E+81 -19.36 121500.0 !2003 Miller&Klippenstein 2003
PLOG / 0.0395 5.62E+81 -19.36 121500.0/
PLOG / 1.0000 1.45E+45 -8.90 96999.0/
PLOG / 10.0000 2.95E+31 -4.97 88465.0/
C3H3+C3H3=A1-+H 1.0467E+54 -11.88 28757. !2003 Miller&Klippenstein 2003
PLOG /0.03947 1.0467E+54 -11.88 28757./
PLOG /1. 1.6975E+48 -9.977 36755./
PLOG /10. 3.6712E+26 -3.879 28963./
fulvene+H=A1+H 4.94E+18 -1.28 5411 !Ahren W. Jasper 2013
PLOG/ 0.00132 4.94E+18 -1.28 5411/
PLOG/ 0.0132 2.15E+22 -2.28 8429/
PLOG/ 0.132 5.60E+26 -3.47 12818/
PLOG/ 1.000 1.66E+25 -2.99 13691/
PLOG/ 1.312 5.06E+25 -3.12 14226/
PLOG/ 13.12 2.20E+27 -3.48 19199/
fulvene=A1-+H 2.57E+97 -23.2 153470.0 !2003 Miller&Klippenstein 2003
PLOG / 0.0395 2.57E+97 -23.2 153470.0/
PLOG / 1.0000 2.24E+68 -14.7 142570.0/
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    PLOG / 10.0000 8.51E+24 -2.5 113330.0/
    !*********************************** Reactions of A1- *****************************
A1-(+M)=o-C6H4+H(+M) 4.300E+12 0.616 77313. !RRKM 00-HAI-FRE
    LOW/ 1.000E+84 -18.866 90064/ !20130218
    TROE/ 0.902 696. 358. 3856. /
    H2/2.0/ CH4/2.0/
    n-C6H5 = A1- 3.70E+63 -16.49 36100. !1997Wang&Frenklach RRKM
    PLOG/ 0.013 3.70E+63 -16.49 36100./
    PLOG/ 0.026 1.30E+62 -15.94 35800./
    PLOG/ 0.118 1.30E+59 -14.78 35600./
    PLOG/ 1.00 5.10E+54 -13.11 35700./
    PLOG/ 10.00 3.50E+46 -10.44 33600./
    n-C6H5 = o-C6H4 + H 1.60E+65 -16.00 58400. !1997Wang&Frenklach RRKM
    PLOG/ 0.013 1.60E+65 -16.00 58400./
    PLOG/ 0.026 2.70E+65 -15.93 59700./
    PLOG/ 0.118 1.50E+64 -15.32 61500./
    PLOG/ 1.00 1.30E+59 -13.56 62000./
    PLOG/ 10.00 1.10E+50 -10.69 60900./
    n-C6H5+H = C4H4+C2H2 1.60E+19 -1.60 2220.0 !1997Wang&Frenklach RRKM
    PLOG/ 0.026 1.60E+19 -1.60 2220.0/
    PLOG/ 0.118 1.30E+20 -1.85 2960.0/
    PLOG/ 1.00 6.30E+25 -3.34 10014.0/
    A1-=nC4H3+C2H2 3.55E+78 -17.787 137467.2 !1997 Madden et al. RRKM
    PLOG / 0.500 3.55E+78 -17.787 137467.2/
    PLOG / 1.000 3.92E+74 -16.6 135581.1/
    PLOG / 10.000 1.79E+61 -12.663 128678.3/
    nC4H3+C2H2=o-C6H4+H 1.90E+36 -7.21 17900.0 !1994 Wang&Frenklach RRKM
    PLOG / 0.0132 9.20E+33 -6.57 15900.0/
    PLOG / 0.0263 1.90E+36 -7.21 17900.0/
    PLOG / 0.1184 3.50E+41 -8.63 23000.0/
    PLOG / 1.0000 6.90E+46 -10.01 30100.0/
    PLOG / 10.0000 3.10E+49 -10.59 37700.0/
    A1-+H=o-C6H4+H2 2.36E-06 5.80 11714 !2001 A. M. Mebel and M.C.Lin
    PLOG/ 0.132 2.36E-06 5.80 11714/
    PLOG/ 1.000 1.16E-14 8.13 8766/
    PLOG/ 10.00 2.58E-22 10.22 5350/
    l-C6H4+H=A1- 4.00E+77 -19.99 28100.0 !1994 Wang&Frenklach RRKM
    plog / 0.0132 4.40E+74 -19.09 25800.0/
    plog / 0.0263 4.00E+77 -19.99 28100.0/
    plog / 0.1184 4.70E+78 -20.10 29500.0/
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plog / 1.0000 1.70E+78 -19.72 31400.0/
plog / 10.0000 3.90E+69 -16.63 34100.0/
!****************************************** Reactions of cC5H5-13E5M(Methylcyclopentadiene)**
C5H5+CH3=>cC5H5-13E5M 9.10E+109 -29.19 41906 !Sandeep Sharma and William H. Green J. Phys. Chem. A 2009, 113, 8871-8882
PLOG/ 0.01 9.10E+109 -29.19 41906/
PLOG/ 1.00 3.06E+105 -27.05 47952/
PLOG/ 10.0 2.38E+94 -23.52 45184/
PLOG/ 100 1.09E+70 -16.33 32296/
C5H5+CH3=>fulvene+H2 9.25E+01 2.19 8815 !Sandeep Sharma and William H. Green J. Phys. Chem. A 2009, 113, 8871-8882
PLOG/ 0.01 9.25E+01 2.19 8815 /
PLOG/ 1.00 1.14E+15 -1.40 20266 /
PLOG/ 10.0 3.62E+31 -5.90 35631 /
PLOG/ 100 3.38E+43 -9.05 49742 /
cC5H5-13E5M=>C5H5+CH3 4.49E+77 -19.26 89496 !Sandeep Sharma and William H. Green J. Phys. Chem. A 2009, 113, 8871-8882
PLOG/ 0.01 4.49E+77 -19.26 89496/
PLOG/ 1.00 2.01E+89 -21.78 105380/
PLOG/ 10.0 6.89E+84 -20.17 106554/
PLOG/ 100 4.46E+71 -16.16 100961/
cC5H5-13E5M=>fulvene+H2 3.38E+77 -21.53 96791 !Sandeep Sharma and William H. Green J. Phys. Chem. A 2009, 113, 8871-8882
PLOG/ 0.01 3.38E+77 -21.53 96791/
PLOG/ 1.00 2.04E+94 -25.05 118602/
PLOG/ 10.0 1.05E+97 -25.23 126838/
PLOG/ 100 3.85E+84 -21.21 124346/
C5H5+CH3=>C5H5CH2-2+H 7.49E+13 -0.30 11640 !Sandeep Sharma and William H. Green J. Phys. Chem. A 2009, 113, 8871-8882
PLOG/ 0.01 7.49E+13 -0.30 11640/
PLOG/ 1.00 7.93E+27 -4.14 24060/
PLOG/ 10.0 7.18E+44 -8.75 40084/
PLOG/ 100 1.31E+53 -10.86 51760/
C5H5+CH3=>C5H5CH2-3+H 2.18E+14 -0.40 17024 !Sandeep Sharma and William H. Green J. Phys. Chem. A 2009, 113, 8871-8882
PLOG/ 0.01 2.18E+14 -0.40 17024/
PLOG/ 1.00 1.31E+23 -2.81 24726/
PLOG/ 10.0 6.08E+38 -7.08 39076/
PLOG/ 100 1.81E+52 -10.67 54105/
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C5H5+CH3=>C5H5CH2-1+H 8.13E+25 -3.51 41018 !Sandeep Sharma and William H. Green J. Phys. Chem. A 2009, 113, 8871-8882

PLOG/ 0.01 8.13E+25 -3.51 41018/

PLOG/ 1.00 3.83E+26 -3.69 41579/

PLOG/ 10.0 1.16E+33 -5.47 47110/

PLOG/ 100 1.03E+48 -9.54 61181/

cC5H5-13E5M=>C5H5CH2-2+H 1.38E+96 -24.49 116744 !Sandeep Sharma and William H. Green J. Phys. Chem. A 2009, 113, 8871-8882

PLOG/ 1.00 1.38E+96 -24.49 116744/

PLOG/ 10.0 1.54E+98 -24.53 124128/

PLOG/ 100 3.13E+86 -20.76 121667/

cC5H5-13E5M=>C5H5CH2-3+H 1.61E+100 -25.89 121934 !Sandeep Sharma and William H. Green J. Phys. Chem. A 2009, 113, 8871-8882

PLOG/ 1.00 1.61E+100 -25.89 121934/

PLOG/ 10.0 2.05E+103 -26.14 130620/

PLOG/ 100 7.82E+93 -22.94 130454/

cC5H5-13E5M=>C5H5CH2-1+H 9.33E+109 -29.66 135070 !Sandeep Sharma and William H. Green J. Phys. Chem. A 2009, 113, 8871-8882

PLOG/ 1.00 9.33E+109 -29.66 135070/

PLOG/ 10.0 1.07E+116 -30.36 147389/

PLOG/ 100 1.21E+114 -28.95 154902/

C5H5CH2-2=fulvene+H 1.35e+58 -13.11 73890 !Polimi V2012

C5H5CH2-2=A1+H 9.25e+43 -9.19115 55756.8 !Polimi V2012

cC5H5-13E5M+H=C5H5CH2-2+H2 1.30e+06 2.38 2800.00 !Polimi V2012

C5H5CH2-1=C5H5CH2-2 1.69e+30 -5.9432 21537.5 !Polimi V2012

C5H5CH2-2=C5H5CH2-3 1.08e+41 -8.73397 44399 !Polimi V2012

C5H5CH2-3=fulvene+H 3.67e+43 -9.19 57330 !Polimi V2012

C5H5CH2-1=C5H5CH2-3 9.23e+27 -5.12362 28314.7 !Polimi V2012

C5H5CH2-3=A1+H 1.38e+46 -9.72349 57338 !Polimi V2012

C5H5CH2-1=fulvene+H 1.07e+29 -5.32 32810 !Polimi V2012

C5H5CH2-1=A1+H 1.98e+31 -6.06562 20629.6 !Polimi V2012

H+cC5H5-13E5M=>CH3+C5H6 1.500E+13 0.0 2000.0 !Polimi V2012

CH3+cC5H5-13E5M=>CH4+A1+H 3.903E+05 2.0 3544.16 !Polimi V2012

C2H5+cC5H5-13E5M=>C2H6+A1+H 2.298E+05 2.0 6224.33 !Polimi V2012

C5H5+CH3=>cC5H5-13E1M 9.10E+109 -29.19 41906 !Sandeep Sharma and William H. Green J. Phys. Chem. A 2009, 113, 8871-8882

PLOG/ 0.01 9.10E+109 -29.19 41906/

PLOG/ 1.00 3.06E+105 -27.05 47952/

PLOG/ 10.0 2.38E+94 -23.52 45184/

PLOG/ 100 1.09E+70 -16.33 32296/

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cC5H5-13E1M=>C5H5+CH3 4.49E+77 -19.26 89496 !Sandeep Sharma and William H. Green J. Phys. Chem. A 2009, 113, 8871-8882
PLOG/ 0.01 4.49E+77 -19.26 89496/
PLOG/ 1.00 2.01E+89 -21.78 105380/
PLOG/ 10.0 6.89E+84 -20.17 106554/
PLOG/ 100 4.46E+71 -16.16 100961/
H+cC5H5-13E1M=>CH3+C5H6 1.500E+13 0.0 2000.0 !Polimi V2012
!************************************* Reactions of C5H5(1,3-Cyclopentadienyl) and C5H6(1,3-cyclopentadiene) **********************************************************
C3H3+C2H2=>C5H5 6.17E+66 -15.7 47729 !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 0.132 6.17E+66 -15.7 47729/ !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 1.000 6.87E+55 -12.5 42000/ !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 10.00 1.13E+43 -8.80 34983/ !L. V. Moskaleva, M. C. Lin 1999
C5H5=>C3H3+C2H2 2.79E+79 -18.3 130768 !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 0.132 2.79E+79 -18.3 130768/ !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 1.000 1.98E+68 -15.0 124824/ !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 10.00 5.70E+54 -11.10 116874/ !L. V. Moskaleva, M. C. Lin 1999
C5H5=lC5H5 2.25E+108 -28.2 127755 !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 0.132 2.25E+108 -28.2 127755/ !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 1.000 1.21E+109 -28.1 130355/ !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 10.00 2.08E+112 -28.6 136922/ !L. V. Moskaleva, M. C. Lin 1999
C5H5=C5H52 5.17E+80 -20.4 96136 !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 0.132 5.17E+80 -20.4 96136/ !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 1.000 5.92E+78 -19.5 96640/ !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 10.00 1.32E+78 -19.0 99133/ !L. V. Moskaleva, M. C. Lin 1999
C3H3+C2H2=>lC5H5 6.87E+71 -18.2 45334 !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 0.132 6.87E+71 -18.2 45334/ !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 1.000 4.11E+72 -18.2 45411/ !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 10.00 1.55E+77 -19.1 49598/ !L. V. Moskaleva, M. C. Lin 1999
lC5H5=>C3H3+C2H2 3.12E+82 -20.6 68862 !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 0.132 3.12E+82 -20.6 68862/ !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 1.000 1.95E+83 -20.6 68951/ !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 10.00 5.61E+87 -21.5 73148/ !L. V. Moskaleva, M. C. Lin 1999
C3H3+C2H2=>C5H52 1.34E+68 -16.9 51542 !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 0.132 1.34E+68 -16.9 51542/ !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 1.000 2.70E+53 -12.6 41445/ !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 10.00 1.81E+35 -7.6 76409/ !L. V. Moskaleva, M. C. Lin 1999
C5H52=>C3H3+C2H2 3.40E+80 -19.2 102213 !L. V. Moskaleva, M. C. Lin 1999
PLOG/ 0.132 3.40E+80 -19.2 102213/ !L. V. Moskaleva, M. C. Lin 1999
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PLOG/ 1.000 7.48E+65 -15.0 92200/ !L. V. Moskaleva, M. C. Lin 1999

PLOG/ 10.00 4.57E+47 -9.9 51542/ !L. V. Moskaleva, M. C. Lin 1999

C5H5+H(+M)=C5H6(+M) 1.000E+14 0.000 0.00 !92-EMD-BRE, est., 94-FRA-HER

LOW / 4.400E+80 -18.280 12994.0/ !96-DAV-WAN, 97-WAN-FRE

TROE / 0.068 400.7 4135.8 5501.9 /

H2/2.0/ CH4/2.0/

C5H6(+M)= aC3H4+C2H2(+M) 3.8E+17 0.0 1.04E+05 !Mackie et al. 2001 PCCP

LOW /1.00E+98 -22.25 126321.5/

TROE /1.440547E-01 5.357622E+00 3.283766E+03 6.710101E+09/

H2 /2.0/ CH4 /2.0/

C5H6+H=C5H5+H2 7.2E+13 0 3500.0 !Better for C5H6 flow reactor pyrolysis

C5H6+H=C2H2+aC3H5 7.74E+36 -6.2 32890.0 !zhong & bozzeli j phys chem a 102 ! sensitive reaction better for C5H6 flow reactor pyrolysis

C5H6+C2H3=C5H5+C2H4 6.00E+12 0.0 0.0 !2001 Bacskay&Mackie 6.00E+12

C5H6+CH3=C5H5+CH4 0.18 4.0 0.0 !zhong & bozzeli j phys chem a 102: 3537 1998

aC3H5+C2H2=lC5H7 3.0e+11 0.0 6883.4 !ziegler et al. j. anal.apply.pyrolysis 73 212-230 (2005)

C5H6+H=lC5H7 2.4e+73 -17.85 31500.0 !

lC5H5+H=C5H4+H2 1.81E+12 0.0 0.0 !1986 Tsang&Hampson C2H5+H in 2002 Richter&Howard

lC5H5+CH3=C5H4+CH4 1.95E+13 -0.50 0.0 !1986 Tsang&Hampson C2H5+CH3 in 2002 Richter&Howard

aC3H5+C2H3=lC5H7+H 1.00E+13 0.0 0.0 !USC Mech II Est.

C5H5+aC3H4=A1+C2H3 2E+10 0 0 !EST

C5H5+pC3H4=A1+C2H3 2E+10 0 0 !EST

C4H5-2+C2H4=C5H6+CH3 5.00E+14 0.0 25000.0 ! USC Mech V2.0

!!!!*** mechanism for cyclopentadiene decomposition ** C5H6+C5H5=>
1.574E+25 -3.935 23108 !Carlo Cavallotti 2012 JPCA

C5H6+C5H5=>A1+nC4H5 7.430E+29 -4.515 40873 !Carlo Cavallotti 2012 JPCA

CH3+nC4H3=>C5H6 1.000E+13 0.0 0.0 !Polimi V2012

C3H3+C2H4=H+C5H6 5.000E+10 0.0 20400.0 !Polimi V2012

CH3+C4H2=>C5H5 1.000E+11 0.0 7600.0 !Polimi V2012

CH3+C5H5=nC4H5+C2H3 1.000E+12 0.0 3000.0 !Polimi V2012

CH3+C5H5=>C4H6+C2H2 1.500E+12 0.0 3000.0 !Polimi V2012

C2H3+aC3H4=>C5H6+H 5.000E+11 0.0 3000.0 !Polimi V2012

C2H3+pC3H4=>C5H6+H 5.000E+11 0.0 3000.0 !Polimi V2012

C5H5+C5H6=>A1C2H3+C2H3 3.000E+55 -11.390 66311.0 !Polimi V2012

C5H5+C5H6=>C9H7+CH4 5.000E+01 3.100 14800.0 !Polimi V2012

C5H5+C5H6=>0.5A1+0.5nC4H5+0.5A1C2H3+0.5C2H3 5.250E+16 -1.407 23454.0 !Polimi V2012

C5H5+C5H6=>A1CH2+0.5aC3H4+0.5pC3H4 1.000E+12 .000 25000.0 !Polimi V2012

aC3H5+C5H6=>C3H6+C5H5 2.407E+05 2.0 15253.34 !Polimi V2012

nC4H5+C5H6=>aC3H5+A1 1.000E+12 0.00 5000.0 !Polimi V2012

!************************************ Reactions of C6H4 ********************************

o-C6H4=C4H2+C2H2 6.50E+13 0.0 83000.0 !1999 Moskaleva et al. RRKM

PLOG / 0.1315 1.95E+90 -21.3 139396.2/

PLOG / 1.0000 2.07E+85 -19.6 138901.4/

PLOG/ 5.000 7.89E+75 -16.8 134903.4/

PLOG / 10.0000 7.89E+75 -16.8 134903.4/

l-C6H4 + H = o-C6H4+ H 8.70E+45 -9.61 22300. !1997 Wang&Frenklach

PLOG/ 0.013 8.70E+45 -9.61 22300./

PLOG/ 0.026 2.20E+47 -9.98 24000./

PLOG/ 0.118 9.70E+48 -10.37 27000./

PLOG/ 1.000 1.40E+54 -11.70 34500./

PLOG/ 10.00 5.70E+55 -11.98 41900./

l-C6H4+H=C6H3+H2 1.33E+06 2.5 9240.0 !USC Mech II

C3H2+C3H2=l-C6H4 3.00E+11 0.0 0.0 !1987 Wu&Kern C3H3+C3H3=A1

C4H2+C2H2=l-C6H4 4.47E+11 0.0 30010.0 !1986 Chanmugathas&Heicklen C4H4+C2H2=A1 in 2002 Richter&Howard

nC4H3+C2H2=l-C6H4+H 3.70E+16 -1.2 11100.0 !1997 Wang&Frenklach RRKM 20Torr

C4H4+C2H=l-C6H4+H 1.20E+13 0.0 0.0 !USC Mech II

C6H3+H=l-C6H4 4.20E+44 -10.27 7890.0 !1Wang&Frenklach RRKM iC4H3+H=C4H4 in 1997 Wang&Frenklach

PLOG / 0.0263 4.20E+44 -10.27 7890.0/

PLOG / 0.1184 5.30E+46 -10.68 9270.0/

PLOG / 1.0000 3.40E+43 -9.01 12120.0/

C4H2+C2H=C6H3 1.10E+30 -6.30 2790.0 !1997 Wang&Frenklach RRKM

PLOG / 0.0263 1.10E+30 -6.30 2790.0/

PLOG / 0.1184 1.30E+30 -6.12 2510.0/

PLOG / 1.0000 4.50E+37 -7.68 7100.0/

C6H2+H=C6H3 4.30E+45 -10.15 13250.0 !1997 Wang&Frenklach RRKM C4H2+H=iC4H3 in 1997 Wang&Frenklach

PLOG / 0.0263 4.30E+45 -10.15 13250.0/

PLOG / 0.1184 2.60E+46 -10.15 15500.0/

PLOG / 1.0000 1.10E+30 -4.92 10800.0/

C6H3+H=C4H2+C2H2 2.40E+19 -1.6 2800.0 !1997 Wang&Frenklach RRKM 20Torr iC4H3+H=C2H2+C2H2 in 1997 Wang&Frenklach

o-C6H4+C3H3=>C7H5+C2H2 6.93E+59 -12.732 53252 !Akira Matsugi and Akira Niyoshi 2012 PCCP,14.

PLOG/ 0.0132 6.93E+59 -12.732 53252/

PLOG/ 0.132 4.36E+61 -13.054 61485/

PLOG/ 1.000 9.61E+54 -11.098 61937/

PLOG/ 10.00 2.58E+38 -6.427 55219/

PLOG/ 100.0 3.29E+15 -0.001 45393/

C7H5+C2H2=>o-C6H4+C3H3 4.68E+61 -13.236 79195 !Akira Matsugi and Akira Niyoshi 2012 PCCP,14.

PLOG/ 0.0132 4.68E+61 -13.236 79195/

PLOG/ 0.132 2.76E+63 -13.551 87406/

PLOG/ 1.000 5.74E+56 -11.587 87838/

PLOG/ 10.00 1.44E+40 -6.908 81096/

PLOG/ 100.0 1.81E+17 -0.480 71271/

o-C6H4+C3H3=>C9H7 7.46E+100 -25.035 61535.403 !Akira Matsugi and Akira Niyoshi 2012 PCCP,14. 20130823

PLOG/ 0.0132 1.49E+100 -25.035 61535.403/ !/5

PLOG/ 0.132 1.12E+79 -18.907 49031.8081 / !/5

PLOG/ 1.000 7.14E+57 -12.867 34883.772 / !/5

PLOG/ 10.00 1.12E+37 -6.994 20138.245 / !/5

PLOG/ 100.0 6.12E+24 -3.553 11067.3913 / !/5

C9H7=>o-C6H4+C3H3 5.46E+121 -29.395 199434.5939

PLOG/ 0.0132 8.44E+108 -29.395 199434.5939 /

PLOG/ 0.132 4.77E+92 -25.566 193628.3812 /

PLOG/ 1.000 9.17E+71 -20.893 183479.1826 /

PLOG/ 10.00 3.91E+54 -15.042 168832.8069 /

PLOG/ 100.0 2.35E+78 -10.189 155667.9384 /

!*** reactions of C5H2 C5H3 cC5H4(cyclopenta
** C4H2+CH2*=C5H3+H
1.30E+13 0.0 0.0 !1992 Miller&Melius

C4H2+CH2=C5H3+H 3.00E+13 0.0 0.0 !1992 Miller&Melius

C4H2+CH=C5H2+H 1.00E+14 0.0 0.0 !1992 Miller&Melius

C5H3+H=C5H2+H2 6.03E+13 0.0 15103.0 !1992 Baulch et al. CH3+H=CH2+H2 in 2002 Richter&Howard

C5H3+CH3=A1 4.3E+12 0.0 0.0 !Estimated

C5H3+CH=C6H2+H+H 5.00E+13 0.0 0.0 ! Estimated

C5H3+CH2=l-C6H4+H 5.00E+13 0.0 0.0 ! = C3H3+CH2

cC5H4=C5H4 1.98E+12 0.56 42240.0

PLOG / 0.1 2.30E+39 -8.81 47800.0 / != cC3H4 = aC3H4 99DAV/LAW RRKM

PLOG / 0.4 7.59E+40 -9.07 48831.0 /

PLOG / 1 4.89E+41 -9.17 49594.0 /

PLOG / 2 8.81E+41 -9.15 50073.0 /

PLOG / 5 4.33E+41 -8.93 50475.0 /

PLOG / 10 7.20E+40 -8.60 50600.0 /

PLOG / 100 1.60E+35 -6.64 49500.0 /

cC5H4+H=>C5H5 6.61E+12 0.3 770 ! Marco Derudi, Daniela Polino and Carlo Cavallotti PCCP 2011,13

C5H5=>cC5H4+H 5.37E+17 -0.55 115500 ! Marco Derudi, Daniela Polino and Carlo Cavallotti PCCP 2011,13

cC5H4+A1CH3=C5H5+A1CH2 4.47E+03 2.37 3300 ! Marco Derudi, Daniela Polino and Carlo Cavallotti PCCP 2011,13

C4H2+CH3=C5H4+H 2.40E+09 0.91 20700.0 !1999 Davis et al. C2H2+CH3=aC3H4+H in 2010 Li(Ph.D. Thesis)

C4H+CH4=C5H4+H 2.40E+09 0.91 20700.0 !1999 Davis et al. C2H2+CH3=aC3H4+H in 2010 Li(Ph.D. Thesis)

aC3H4+C2H=C5H4+H 9.60E+13 0.0 0.0 !2000 Appel et al. C2H2+C2H=C4H2+H in 2010 Li(Ph.D. Thesis)

C5H3+H=C5H4 3.6308E+36 -7.36 6039. !2008 Miller & Senosiain & Klippenstein C3H3+H=pC3H4 20130821

PLOG /0.03947 7.26E+36 -7.36 6039./ !*2

PLOG /1. 1.59E+30 -5.06 4861./ !*2

PLOG /10. 2.14E+24 -3.15 3261./ !*2

C5H4+H=C5H3+H2 1.00E+06 2.50 5000.0 !Alzueta et al. 1998

!*** Reactions of CnH2************************

C4H+H(+M) = C4H2(+M) 1.000E+17 -1.000 0.00 != C2H +H

LOW / 3.750E+33 -4.800 1900.00 /

TROE/ 0.6464 132.00 1315.00 5566.0 /

C4H+H2 = H+C4H2 4.90E+05 2.500 560.00

C4H2+C2H=C6H2+H 9.60E+13 0.0 0. != C2H2 + C2H HACA

C2H2+C4H=C6H2+H 7.80E+13 0.0 0. != C2H2 + C2H

C4H+C2H=C6H2 5.00E+13 0.0 0.0 != C2H+C2H

C3H2+C3H2=C6H2+H2 1.00E+13 0.0 0.0 !MODIF

!C6H2+C2H=C8H2+H 9.60E+13 0.0 0. != C2H2 + C2H HACA

! Submechanism of PAH !************************************* **********************

A1C2H-=C6H3C2H+H 6.11E+45 -8.857 94350.6 !1997 Madden et al. RRKM A1-=o-C6H4+H

plog / 0.500 6.11E+45 -8.857 94350.6/

plog / 1.000 8.00E+41 -7.72 92300.3/

plog / 10.000 1.66E+30 -4.318 85756.9/

A1C2H-=C6H3+C2H2 3.55E+78 -17.787 137467.2 !1997 Madden et al. RRKM A1-=nC4H3+C2H2

plog / 0.500 3.55E+78 -17.787 137467.2/

plog / 1.000 3.92E+74 -16.6 135581.1/

plog / 10.000 1.79E+61 -12.663 128678.3/

A1C2H-+H=C6H3C2H+H2 4.40E-13 7.831 9261.0 !2001 Mebel et al. A1-+H=o-C6H4+H2

A1C2H-=nC4H3+C4H2 3.55E+78 -17.787 137467.2 !1997 Madden et al. RRKM A1-=nC4H3+C2H2

plog / 0.500 3.55E+78 -17.787 137467.2/

plog / 1.000 3.92E+74 -16.6 135581.1/

plog / 10.000 1.79E+61 -12.663 128678.3/

C6H3C2H=C4H2+C4H2 1.95E+90 -21.3 139396.2 !refer to 1999 Moskaleva et al. o-C6H4=C4H2+C2H2

PLOG / 0.1315 1.95E+90 -21.3 139396.2/

PLOG / 1.0000 2.07E+85 -19.6 138901.4/

PLOG/ 5.000 7.89E+75 -16.8 134903.4/

PLOG / 10.0000 7.89E+75 -16.8 134903.4/

!********************************** Reactions of A1C2H (Phenylacetylene) **

A1C2H-+H(+M)=A1C2H(+M) 1.00E+14 0.0 0.0 !1997 Wang&Frenklach A1-+H(+M)=A1(+M in 1997 Wang&Frenklach

LOW / 6.60E+75 -16.30 7000.0/

TROE/ 1.0 0.1 584.9 6113.0/

H2/2.0/ CH4/2.0/ C2H6/3.0/

! shield in this work, the estimation to toluene is not adeqate.

!A1C2H(+m)=A1-+C2H(+m) 7.80e+27 -3.16 1.07447e+05 !estimated from Klippenstein 2007

! LOW/4.00E+98 -22.966 1.2208E+05/

! TROE/7.054562E-01 9.999989E+09 4.599180E+02 8.213938E+09/

A1C2H(+M)=A1CC+H(+M) 2.78E+15 0.17 9.1168E+04 !estimated from 2007 Kliphenstein et al. A1CH3(+M) = A1CH2+H(+M)

LOW/1.00E+98 -22.855 9.9882E+04/

TROE/6.547194E-02 1.511253E+01 9.999996E+09 7.596123E+07/

A1C2H+H=A1cC2H2+H 2.30E+15 -0.26 7600.0 !1999 Davis et al. pC3H4+H=aC3H4+H 0.1atm

A1+C2H=A1C2H+H 5.00E+13 0.0 0.0 !1997 Wang&Frenklach

A1C2H+H=A1CC+H2 2.50E+14 0.0 16000.0 !1985 Kiefer et al. A1+H=A1-+H2 in 1997 Wang&Frenklach

A1C2H+H=A1C2H-+H2 1.084e17 -0.70 20011.2 !refa A1+H=A1-+H2 *5/6

A1-+C2H2=A1C2H+H 2.66E+32 -5.3 23786.9 !I.V. Tokmakov, M.C. Lin, J. Am. Chem. Soc. 125(2003) 11397-11408.

A1-+C4H4=A1C2H+C2H3 3.20E+11 0.0 1350.0 !1988 Harris et al.

nC4H5+C4H2=A1C2H+H 3.16E+11 0.0 1800.0 !1984 Cole et al.

!********************************* Reactions of A1C2H2 ****************************** A1-+C2H3=A1CCH2+H 1.80E+31 -4.63 31652. !1997 Wang&Frenklach RRKM

PLOG/ 0.026 1.80E+31 -4.63 31652./

PLOG/ 0.118 5.80E+18 -1.00 26852./

PLOG/ 1.000 8.50E-02 4.71 18424./

A1-+C2H3=A1CHCH+H 1.50E+32 -4.91 35504. !1997 Wang&Frenklach RRKM

PLOG/ 0.026 1.50E+32 -4.91 35504./

PLOG/ 0.118 5.10E+20 -1.56 31412./

PLOG/ 1.000 9.40E+00 4.14 23234./

A1CHCH+H=A1CCH2+H 2.30E+37 -6.00 35164. !1997 Wang&Frenklach RRKM

PLOG/ 0.026 2.30E+37 -6.00 35164./

PLOG/ 0.118 1.20E+25 -2.42 30530./

PLOG/ 1.000 9.90E+04 3.37 22040./

A1-+C2H2=A1CHCH 7.70E+40 -9.19 13400.0 !1994 Wang&Frenklach RRKM

plog / 0.0132 4.00E+39 -8.94 12000.0/

plog / 0.0263 7.70E+40 -9.19 13400.0/

plog / 0.1184 9.90E+41 -9.26 15700.0/

plog / 1.0000 7.00E+38 -8.02 16400.0/

plog / 10.0000 7.90E+29 -5.15 13700.0/

A1C2H+H=A1CHCH 1.00E+54 -12.76 17185.0 !1997 Wang&Frenklach RRKM

plog / 0.0263 1.00E+54 -12.76 17185.0/

plog / 0.1184 1.20E+51 -11.69 17300.0/

plog / 1.0000 3.00E+43 -9.22 15300.0/

A1C2H+H=A1CCH2 1.00E+54 -12.76 17185.0 !1997 Wang&Frenklach RRKM A1C2H+H=A1CCH2 in 1997 Wang&Frenklach

plog / 0.0263 1.00E+54 -12.76 17185.0/

plog / 0.1184 1.20E+51 -11.69 17300.0/

plog / 1.0000 3.00E+43 -9.22 15300.0/

A1CHCH+H=A1C2H+H2 3.00E+13 0.0 0.0 !GRI C2H3+H=C2H2+H2in 1997 Wang&Frenklach

A1CCH2+H=A1C2H+H2 3.00E+13 0.0 0.0 !GRI C2H3+H=C2H2+H2 in 1997 Wang&Frenklach

A1CHCH=C6H4C2H3 6.40E+61 -14.59 88200.0 !1999 Davis et al. pC3H4=aC3H4

plog / 0.100 6.40E+61 -14.59 88200.0/

plog / 0.400 5.81E+62 -14.63 91211.0/

plog / 1.000 5.15E+60 -13.93 91117.0/

plog / 2.000 7.64E+59 -13.59 91817.0/

plog / 5.000 3.12E+58 -13.07 92680.0/

plog / 10.000 1.90E+57 -12.62 93300.0/

plog /100.000 1.40E+52 -10.86 95400.0/

A1CHCH+H=C6H4C2H3+H 2.30E+37 -6.00 35164.0 !1997 Wang&Frenklach A1CHCH+H=A1CCH2+H

C6H4C2H3=o-C6H4+C2H3 6.11E+45 -8.857 94350.6 !1997 Madden et al. RRKM A1-=o-C6H4+H

plog / 0.500 6.11E+45 -8.857 94350.6/

plog / 1.000 8.00E+41 -7.72 92300.3/

plog / 10.000 1.66E+30 -4.318 85756.9/

!** Reactions of A1C2H3 *******************

C6H4C2H3+H(+M)=A1C2H3(+M) 1.00E+14 0.0 0.0 !1997 Wang&Frenklach A1-+H(+M)=A1(+M)

LOW / 6.60E+75 -16.30 7000.0/

TROE/ 1.0 0.1 584.9 6113.0/

H2/2.0/ CH4/2.0/ C2H6/3.0/

A1+C2H3=A1C2H3+H 7.90E+11 0.0 6400.0 !1989 Fahr&Stein

A1-+C2H4=A1C2H3+H 2.51E+12 0.0 6190.0 !1989 Fahr&Stein in 1997 Wang&Frenklach

A1-+C2H3=A1C2H3 1.90E+48 -10.52 17489.0 !1997 Wang&Frenklach RRKM

plog / 0.0263 1.90E+48 -10.52 17489.0/

plog / 0.1184 3.90E+38 -7.63 12900.0/

plog / 1.0000 1.20E+27 -4.22 7200.0/

C4H4+C4H4=A1C2H3 1.50E+14 0.0 38000.0 !1984 Lundgard&Heicklen

A1C2H3=A1CCH2+H 1.20E+46 -9.07 118323.0 !1997 Wang&Frenklach RRKM

plog / 0.0263 1.20E+46 -9.07 118323.0/

plog / 0.1184 3.80E+37 -6.55 114200.0/

plog / 1.0000 5.30E+27 -3.63 109300.0/

A1C2H3+H=A1CCH2+H2 3.33E+05 2.53 9240.0 !HACA

A1C2H3=A1CHCH+H 1.90E+54 -11.39 130224.0 !1997 Wang&Frenklach RRKM

plog / 0.0263 1.90E+54 -11.39 130224.0/

plog / 0.1184 1.30E+44 -8.36 125400.0/

```
   plog / 1.0000 1.10E+32 -4.77 119500.0/
   A1C2H3+H=A1CHCH+H2 6.65E+05 2.53 12240.0 !GRI C2H4+H=C2H3+H2
in 1997 Wang&Frenklach
   !**************************************** Reactions of A1C2H4 *************************
A1C2H3+H(+M)=A1CHCH3(+M) 1.367E+09 1.463 1355.0 !2004 Miller&Klippenstein
C2H4+H(+M)=C2H5(+M)
   LOW / 2.027E+39 -6.642 5769.0/
   TROE/-0.569 299.0 9147.0 -152.4/
   H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/
   A1C2H3+H(+M)=A1CH2CH2(+M) 1.367E+09 1.463 1355.0 !2004 Miller&Klippenstein
C2H4+H(+M)=C2H5(+M)
   LOW / 2.027E+39 -6.642 5769.0/
   TROE/-0.569 299.0 9147.0 -152.4/
   H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/
   A1CH2CH2=C2H4+A1- 7.1E+14 0.0 43500.0 !bounaceur et al Int J Chem
Kinet 37: 25-49, 2005 actually taken from Ebert 1978
   A1CHCH3=A1CH2CH2 6.40E+61 -14.59 88200.0 !1999 Davis et al. pC3H4=aC3H4
   plog / 0.100 6.40E+61 -14.59 88200.0/
   plog / 0.400 5.81E+62 -14.63 91211.0/
   plog / 1.000 5.15E+60 -13.93 91117.0/
   plog / 2.000 7.64E+59 -13.59 91817.0/
   plog / 5.000 3.12E+58 -13.07 92680.0/
   plog / 10.000 1.90E+57 -12.62 93300.0/
   plog /100.000 1.40E+52 -10.86 95400.0/
   A1-+C4H6=A1C2H3+C2H3 3.20E+11 0.0 1900.0 !1988 Harris et al.
   !********************************* Reactions of A1C2H5 ***************************
A1C2H5(+m) = A1CHCH3+H(+m) 2.78e+15 0.17 9.1168e+04 !
   LOW/ 1.00E+98 -22.855 9.9882E+04/
   TROE/6.547194E-02 1.511253E+01 9.999996E+09 7.596123E+07/
   A1C2H5(+m) = A1-+C2H5(+m) 1.95E+27 -3.16 1.07447E+05
   LOW/ 1.00E+98 -22.966 1.2208E+05/
   TROE/7.054562E-01 9.999989E+09 4.599180E+02 8.213938E+09/
   A1CH2CH2+H(+M)=A1C2H5(+M) 5.21E+17 -0.990 1580.0 !GRI3.0 C2H5+H(+M)=C2H6(+M)
   LOW / 1.99E+41 -7.080 6685.0/
   TROE/ 0.8422 125.0 2219.00 6882.0/
   H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/
   A1CH2+CH3(+M)=A1C2H5(+M) 6.120E+16 -0.970 620.00 != CH3+CH3(+M)=C2H6(+M)
   LOW / 1.770E+50 -9.670 6220.0/ !
   TROE/ 0.5325 151.0 1038.00 4970.0/
   H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/
```

A1CH2+CH3=A1CHCH3+H 1.730e+039 -7.2310 35366.0 ! Miyoshi 2012

rev / 2.210e+039 -6.8522 24335.7 /

A1CH2+CH3=A1CH2CH2+H 6.348e+032 -5.1046 40697.1 ! Miyoshi 2012

rev / 1.169e+031 -4.6094 14826.4 / A1CH2+CH3=A1-+C2H5 2.028e+033 -5.2232 40498.3 ! Miyoshi 2012

rev / 3.313e+032 -5.4269 14897.5 /

A1CHCH3+H=A1CH2CH2+H 1.614e+024 -2.5623 29906.1 ! Miyoshi 2012

rev / 2.325e+022 -2.4459 15065.6 /

A1CHCH3+H=A1-+C2H5 5.150e+024 -2.6808 29738.4 ! Miyoshi 2012

rev / 6.584e+023 -3.2634 15168.0 /

A1CH2CH2+H=A1-+C2H5 6.974e+014 0.0003 17190.1 ! Miyoshi 2012

rev / 6.181e+015 -0.6985 17459.8 /

A1C2H5+H=A1CHCH3+H2 3.31E+07 2.0 5345.3 !2005 Baulch et al.

A1C2H5+H=A1CH2CH2+H2 7.22E+08 1.50 7412.0 !2005 Baulch et al.

A1C2H5+CH3=A1CHCH3+CH4 1.1E+12 0.0 9100.0 !Bounaceur et al 2005 Int J Chem Kinet 37: 25-49

A1C2H5+CH3=A1CH2CH2+CH4 0.3 4.0 8200.0 !Bounaceur et al 2005 Int J Chem Kinet 37: 25-49

A1C2H5+H=A1+C2H5 1.20E+13 0.0 5100.0 !Ergut et al 2006 Combustion and Flame 144 (2006) 757-772

A1C2H5+H=C6H4C2H5+H2 1.93E+07 2.00 9697.0 !2005 Baulch et al.

!***********IPCH sub mechanism****************this work*******

! IPCH reactions

! isomerization and decomposition of IPCH

IPCH = cC6H11+iC3H7 1.47E+16 0.0 81449.4 !barrierless

IPCH = SXC2H4cC6H11+CH3 4.23E+15 0.0 80690.3 !barrierless!2nd-HR3

IPCH = int1 1.11E+16 0.0 88829.8

IPCH = int2 2.75E+15 0.0 91017.7

IPCH = int3 4.33E+16 0.0 90940.2

int1 = C8H15-1E7M 4.23E+10 0.0 4084.1

int1 = C8H15-3E2M 1.05E+12 0.0 2965.3

int1 = C8H15-2E2M 1.84E+10 0.0 15967.7

int2 = C6H11-1E2IP 3.21E+11 0.0 7516.6

int2 = C6H11-1E5IP 3.51E+11 0.0 6783.7

int3 = C6H11-1E3IP 4.02E+10 0.0 13908.2

int3 = C6H11-1E4IP 9.76E+11 0.0 4949.7

! CH3-abstractions of IPCH

IPCH+H = SXC2H4cC6H11+CH4 1.71E+14 0.0 35590.8

! H-abstractions of IPCH

IPCH+H = PXIPCH+H2 5.86E+14 0.0 13805.7

IPCH+H = TXIPCH+H2 1.61E+14 0.0 8684.7
IPCH+H = T1XIPCH+H2 1.15E+14 0.0 8663.2
IPCH+H = S2XIPCH+H2 4.21E+14 0.0 11389.8
IPCH+H = S3XIPCH+H2 6.40E+14 0.0 11125.9
IPCH+H = S4XIPCH+H2 3.42E+14 0.0 11391.8
IPCH+CH3 = PXIPCH+CH4 7.37E+12 0.0 19247.8
IPCH+CH3 = TXIPCH+CH4 4.23E+12 0.0 14469.2
IPCH+CH3 = T1XIPCH+CH4 2.40E+12 0.0 14369.8
IPCH+CH3 = S2XIPCH+CH4 3.57E+12 0.0 17063.3
IPCH+CH3 = S3XIPCH+CH4 1.45E+13 0.0 16647.6
IPCH+CH3 = S4XIPCH+CH4 8.26E+12 0.0 16918.2
!cyclohexyl radicals
PXIPCH = CH2-IPCH+H 6.00E+13 0.0 36558.5
TXIPCH = CH2-IPCH+H 1.09E+14 0.0 38837.8 !barrierless
TXIPCH = CH2-2-IPCH+H 6.73E+14 0.0 40203.0
T1XIPCH = CH2-2-IPCH+H 5.33E+13 0.0 36975.8
T1XIPCH = IPCH-1E+H 3.04E+14 0.0 37065.3
S2XIPCH = IPCH-1E+H 3.72E+13 0.0 35986.2
S2XIPCH = IPCH-2E+H 2.73E+14 0.0 36898.3
S3XIPCH = IPCH-2E+H 1.88E+14 0.0 37748.9
S3XIPCH = IPCH-3E+H 2.20E+14 0.0 37587.9
S4XIPCH = IPCH-3E+H 2.53E+14 0.0 36087.6
SXC2H4cC6H11 = CH2CHcC6H11+H 2.75E+13 0.0 38245.7 !barrierless
SXC2H4cC6H11 = CH3CHcC6H10+H 2.17E+13 0.0 37820.4
PXIPCH = CH2CHcC6H11+CH3 2.67E+14 0.0 31415.6
PXIPCH = cC6H11+C3H6 1.68E+14 0.0 26950.4
T1XIPCH = CH3CHcC6H10+CH3 1.64E+14 0.0 30616.8
S2XIPCH = cC6H10+iC3H7 0.92+14 0.0 27693.6
TXIPCH = P8XC8H14-2E2M 2.97E+14 0.0 30897.0
T1XIPCH = P6XC6H10-1E2IP 0.75E+14 0.0 31662.1
S2XIPCH = P6XC6H10-1E3IP 0.64E+14 0.0 31111.6
S2XIPCH = P8XC8H14-3E2M 0.69E+14 0.0 30306.8
S3XIPCH = P6XC6H10-1E4IP 1.22E+14 0.0 32524.5
S3XIPCH = S6XC8H14-1E7M 0.73E+14 0.0 29120.4
S4XIPCH = P6XC6H10-1E5IP 1.98E+14 0.0 32204.6
!cyclohexene dissociation
IPCH-1E = C2H4+C4H5-13E2IP 1.87E+15 0.0 65045.0
IPCH-2E = C2H4+C6H9-13E5M 1.15E+15 0.0 62642.5
IPCH-3E = C4H6+C4H7-1E3M 8.08E+14 0.0 64774.8
! alkenes reactions

C8H15-1E7M+H = S3XC8H14-1E7M+H2 2.24E+14 0.0 8247.1

C8H15-1E7M+CH3 = S3XC8H14-1E7M+CH4 4.65E+08 0.0 8374.6

C8H15-1E7M = C3H6+C5H9-1E4M 4.95E+12 0.0 55419.0

C8H15-1E7M = aC3H5+P1XC5H104M 1.33E+14 0.0 63602.3 !barrierless

C8H15-3E2M+H = S5XC8H14-3E2M+H2 2.42E+11 0.0 5397.4

C8H15-3E2M+CH3 = S5XC8H14-3E2M+CH4 3.18E+12 0.0 13386.4

C8H15-3E2M = C3H6+C5H9-2E4M 1.16E+15 0.0 109252.3

C8H15-3E2M = C3H6+C5H9-1E4M 5.73E+12 0.0 56961.1

C8H15-3E2M = nC3H7+P1XC5H8-2E4M 1.90E+15 0.0 68572.3 !barrierless

C8H15-2E2M+H = S4XC8H14-2E2M+H2 2.40E+14 0.0 7480.4

C8H15-2E2M+CH3 = S4XC8H14-2E2M+CH4 1.91E+12 0.0 12610.4

C8H15-2E2M = C4H8-1+C4H7-2E2M 1.95E+15 0.0 108489.2

C8H15-2E2M = C4H8-1+C4H7-1E3M 5.31E+12 0.0 57507.6

C8H15-2E2M = pC4H9+P4XC4H6-2E2M 2.25E+15 0.0 66191.6 !barrierless

C6H11-1E2IP+H = S3XC6H10-1E2IP+H2 1.56E+14 0.0 7994.9

C6H11-1E2IP+CH3 = S3XC6H10-1E2IP+CH4 1.14E+12 0.0 13017.4

C6H11-1E2IP = C3H6+C4H6-1E23M 6.59E+12 0.0 55162.7

C6H11-1E2IP = nC3H7+P1XCH2C4H6-1E3M 2.09E+15 0.0 66986.5 !barrierless

C6H11-1E5IP+H = S3XC6H10-1E5IP+H2 5.10E+15 0.0 11236.2

C6H11-1E5IP+CH3 = S3XC6H10-1E5IP+CH4 4.10E+13 0.0 16489.6

C6H11-1E5IP = C3H6+C4H6-1E23M 1.11E+14 0.0 55272.0

C6H11-1E5IP = aC3H5+P1XC4H723M 3.72E+16 0.0 69110.8 !barrierless

C6H11-1E3IP+H = T3XC6H10-1E3IP+H2 2.22E+14 0.0 8814.2

C6H11-1E3IP+CH3 = T3XC6H10-1E3IP+CH4 1.24E+12 0.0 14405.2

C6H11-1E3IP = C3H6+C5H9-2E4M 3.97E+12 0.0 53586.8

C6H11-1E3IP = C3H6+C6H12-2E 2.91E+13 0.0 55132.9

C6H11-1E3IP = iC3H7+S3XC6H11-1E 6.19E+14 0.0 62634.6 !barrierless

C6H11-1E3IP = nC3H7+S3XC5H8-1E4M 1.65E+14 0.0 64625.7 !barrierless

C6H11-1E4IP+H = S3XC6H10-1E4IP+H2 2.13E+14 0.0 9020.5

C6H11-1E4IP+CH3 = S3XC6H10-1E4IP+CH4 1.24E+12 0.0 14520.7

C6H11-1E4IP = C3H6+C5H9-2E2M 2.55E+15 0.0 104278.3

C6H11-1E4IP = C3H6+C5H9-2E4M 7.33E+12 0.0 57563.2

C6H11-1E4IP = aC3H5+S3XC5H102M 3.20E+14 0.0 63175.1 !barrierless

! Alkyl RAdical reactions

S6XC8H14-1E7M = S7XC8H14-1E7M 8.86E+12 0.0 39591.0

S6XC8H14-1E7M = S5XC8H14-1E7M 5.99E+12 0.0 40073.9

S6XC8H14-1E7M = S4XC8H14-1E7M 3.75E+12 0.0 41288.1

S6XC8H14-1E7M = S3XC8H14-1E7M 1.70E+11 0.0 19827.5

S6XC8H14-1E7M = P8XC8H14-1E7M 5.24E+12 0.0 43070.8

S7XC8H14-1E7M = iC4H8+P5XC5H9-1E 1.61E+15 0.0 64774.8
S6XC8H14-1E7M = CH3+C8H14-16E 5.02E+13 0.0 31473.3
S6XC8H14-1E7M = C4H7-1E3M+C4H7 1.76E+14 0.0 31270.8
S5XC8H14-1E7M = iC3H7+C6H10-15E 1.13E+14 0.0 29438.4
S5XC8H14-1E7M = aC3H5+C5H9-1E4M 2.64E+13 0.0 22944.2
S4XC8H14-1E7M = iC4H9+C5H8-14E 1.43E+14 0.0 31604.4
S4XC8H14-1E7M = C2H3+C6H11-1E5M 1.89E+14 0.0 38619.2
S3XC8H14-1E7M = C4H6+P4XC4H83M 1.12E+15 0.0 39587.0
P8XC8H14-1E7M = CH3+C8H14-17E 2.51E+14 0.0 33953.3
P8XC8H14-1E7M = C3H6+P6XC6H11-1E 2.57E+14 0.0 31562.7
S6XC8H14-1E7M = P1XCH2cC5H85IP 2.09E+10 0.0 7160.5
P8XC8H14-2E2M = S7XC8H14-2E2M 4.25E+13 0.0 40614.4
P8XC8H14-2E2M = S6XC8H14-2E2M 1.62E+13 0.0 40064.0
P8XC8H14-2E2M = S5XC8H14-2E2M 1.97E+12 0.0 23242.3
P8XC8H14-2E2M = S4XC8H14-2E2M 1.50E+11 0.0 13043.8
S7XC8H14-2E2M = C3H6+P5XC5H8-2E2M 1.33E+14 0.0 29919.3
S6XC8H14-2E2M = CH3+C7H11-15E6M 5.43E+13 0.0 31650.1
S6XC8H14-2E2M = C4H8-1+P4XC4H6-2E2M 1.80E+13 0.0 21177.6
S5XC8H14-2E2M = iC4H7-1+C5H10-1E 1.18E+14 0.0 38341.0
S5XC8H14-2E2M = C2H5+C6H9-14E5M 9.41E+13 0.0 30410.1
S4XC8H14-2E2M = nC3H7+C5H7-13E4M 1.31E+15 0.0 40040.1
P8XC8H14-2E2M = C2H4+P6XC6H10-2E2M 3.42E+14 0.0 30662.5
P8XC8H14-3E2M = S7XC8H14-3E2M 2.30E+13 0.0 40525.0
P8XC8H14-3E2M = S6XC8H14-3E2M 1.02E+13 0.0 40827.0
P8XC8H14-3E2M = S5XC8H14-3E2M 8.23E+11 0.0 18331.7
S7XC8H14-3E2M = C3H6+P1XC5H8-2E4M 3.36E+13 0.0 21660.5
S6XC8H14-3E2M = C7H11-14E6M+CH3 8.11E+13 0.0 31922.4
S6XC8H14-3E2M = C4H8-1+S1XC4H6-1E3M 2.46E+14 0.0 39070.3
S5XC8H14-3E2M = C2H5+C6H9-13E5M 4.59E+14 0.0 40185.2
!P8XC8H14-3E2M = C2H4+P1XC6H10-3E5M 2.93E+14 0.0 31433.5
P8XC8H14-3E2M = S1XIPcC5H9 2.24E+11 0.0 8455.7
P6XC6H10-1E5IP = T5XC6H10-1E5IP 4.09E+13 0.0 38585.5
P6XC6H10-1E5IP = S4XC6H10-1E5IP 2.56E+13 0.0 39920.7
P6XC6H10-1E5IP = S3XC6H10-1E5IP 1.27E+12 0.0 17639.2
T5XC6H10-1E5IP = C7H11-15E5M+CH3 1.18E+14 0.0 31177.2
T5XC6H10-1E5IP = C4H6-1E23M+aC3H5 6.05E+13 0.0 21280.9
S4XC6H10-1E5IP = C7H11-14E6M+CH3 4.90E+13 0.0 32027.7
S4XC6H10-1E5IP = C6H10-14E+iC3H7 2.87E+13 0.0 25664.7
S4XC6H10-1E5IP = C5H8-1E34M+C2H3 3.18E+14 0.0 38345.0
S3XC6H10-1E5IP = S2XC4H83M+C4H6 7.87E+14 0.0 38092.6

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P6XC6H10-1E5IP = iC3H7+C6H10-15E 1.16E+14 0.0 25903.2
P6XC6H10-1E5IP = C4H7-1E3M+C4H7 1.56E+14 0.0 29519.9
P6XC6H10-1E5IP = P1XCH2cC5H84IP 2.03E+11 0.0 6033.9
P6XC6H10-1E4IP = T4XC6H10-1E4IP 6.24E+14 0.0 39197.5
P6XC6H10-1E4IP = S5XC6H10-1E4IP 2.09E+15 0.0 42259.8
P6XC6H10-1E4IP = S3XC6H10-1E4IP 2.23E+13 0.0 22254.7
!T4XC6H10-1E4IP = C6H9-14E4Et+CH3 9.21E+13 0.0 31026.2
T4XC6H10-1E4IP = C5H7-14E2IP+CH3 1.30E+14 0.0 31268.6
T4XC6H10-1E4IP = C4H7-1E2IP+C2H3 6.44E+14 0.0 39273.0
S5XC6H10-1E4IP = C6H10-14E+iC3H7 6.17E+13 0.0 26807.3
S5XC6H10-1E4IP = C5H9-2E4M+aC3H5 1.16E+13 0.0 19403.6
S3XC6H10-1E4IP = C6H10-13E+iC3H7 1.82E+14 0.0 33470.4
S3XC6H10-1E4IP = C6H9-13E5M+C2H5 1.36E+14 0.0 37530.3
P6XC6H10-1E4IP = S4XC6H10-1E5M+C2H4 1.18E+14 0.0 31177.2
P6XC6H10-1E4IP = P1XCH2cC5H84IP 1.23E+13 0.0 8551.9
P6XC6H10-1E3IP = T3XC6H10-1E3IP 2.39E+11 0.0 18305.3
P6XC6H10-1E3IP = S5XC6H10-1E3IP 2.81E+13 0.0 40542.9
P6XC6H10-1E3IP = S4XC6H10-1E3IP 4.53E+12 0.0 38309.2
T3XC6H10-1E3IP = C5H7-13E3C3H7+CH3 4.74E+14 0.0 39004.8
T3XC6H10-1E3IP = C4H5-13E2IP+C2H5 3.04E+15 0.0 40562.7
S5XC6H10-1E3IP = S3XC5H8-1E4M+C3H6 4.51E+13 0.0 21133.9
S4XC6H10-1E3IP = C6H11-3E2M+C2H3 1.91E+14 0.0 38627.2
S4XC6H10-1E3IP = C6H10-13E+iC3H7 2.20E+13 0.0 24969.2
S4XC6H10-1E3IP = C5H7-14E3IP+CH3 5.02E+13 0.0 31679.9
P6XC6H10-1E3IP = P4XC4H6-1E3IP+C2H4 1.40E+14 0.0 30376.3
P6XC6H10-1E3IP = P1XCH2cC5H85IP 2.51E+10 0.0 9310.4
P6XC6H10-1E2IP = S5XC6H10-1E2IP 2.41E+13 0.0 40515.0
P6XC6H10-1E2IP = S4XC6H10-1E2IP 9.13E+12 0.0 39644.6
P6XC6H10-1E2IP = S3XC6H10-1E2IP 5.31E+11 0.0 18726.6
S5XC6H10-1E2IP = C3H6+P3XC3H4-1E2IP 4.47E+13 0.0 21378.3
S4XC6H10-1E2IP = C5H7-14E2IP+CH3 7.69E+13 0.0 31805.1
S4XC6H10-1E2IP = C4H8-1+T2XC4H6-1E3M 1.17E+14 0.0 35322.5
S3XC6H10-1E2IP = C4H5-13E2IP+C2H5 5.45E+13 0.0 36155.1
P6XC6H10-1E2IP = C2H4+P4XC4H6-1E2IP 2.70E+14 0.0 30483.6
P6XC6H10-1E2IP = P1XCH2cC5H81IP 3.08E+10 0.0 7584.9
!clyclopantane reactions
S1XIPcC5H9 = T3XcC5H8CH2IP 5.37E+10 0.0 29160.2
T3XcC5H8CH2IP = cC5H7-3ECH2IP+H 8.33E+13 0.0 38714.6
cC5H7-3ECH2IP+H = S2XcC5H6-3ECH2IP+H2 2.42E+14 0.0 8338.9
cC5H7-3ECH2IP+CH3 = S2XcC5H6-3ECH2IP+CH4 4.20E+12 0.0 13266.1
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S2XcC5H6-3ECH2IP = C5H6+iC4H9 7.26E+14 0.0 38611.3
P1XCH2cC5H85IP = S3XcC5H71M5IP 1.12E+12 0.0 25833.6
P1XCH2cC5H85IP = S4XcC5H71M5IP 1.78E+12 0.0 25978.7
S3XcC5H71M5IP = cC5H61M5IP+H 7.27E+13 0.0 38058.9
cC5H61M5IP+H = S1XcC5H65IP+CH4 2.54E+14 0.0 33613.5
S1XcC5H65IP = C5H6+iC3H7 3.23E+14 0.0 34784.0
S4XcC5H71M5IP = cC5H75M+iC3H7 1.31E+14 0.0 26121.7
cC5H75M+H = cC5H7+CH4 6.64E+13 0.0 32210.5
cC5H75M+H = S3XcC5H65M+H2 1.36E+14 0.0 5527.6
cC5H75M+CH3 = S3XcC5H65M+CH4 2.16E+12 0.0 11079.8
S3XcC5H65M = cC5H5-13E5M+H 1.31E+14 0.0 49034.2 !barrierless
P1XCH2cC5H84IP = S3XcC5H71M4IP 1.16E+12 0.0 26229.1
S3XcC5H71M4IP = cC5H74M+iC3H7 1.30E+14 0.0 25487.8
cC5H74M+H = S3XcC5H64M+H2 1.24E+14 0.0 7292.9
cC5H74M+CH3 = S3XcC5H64M+CH4 2.30E+12 0.0 12824.8
S3XcC5H64M = C5H6+CH3 4.34E+14 0.0 39489.6
S3XcC5H64M = cC5H5-13E1M+H 9.76E+13 0.0 45890.4
P1XCH2cC5H81IP = S3XcC5H71M1IP 1.00E+12 0.0 24812.2
S3XcC5H71M1IP = cC5H61M1IP+H 1.02E+14 0.0 38311.2
cC5H61M1IP+H = S2XcC5H51M1IP+H2 4.03E+14 0.0 7510.4
cC5H61M1IP+CH3 = S2XcC5H51M1IP+CH4 3.36E+12 0.0 12659.1
S2XcC5H51M1IP = cC5H5-13E1M+iC3H7 1.46E+14 0.0 32685.5
cC5H5-13E5M = cC5H5-13E1M 1.50E+13 0.0 24466.4
! aromatic reactions
IPCH-1E+H = S6XIPCH-1E+H2 2.69E+14 0.0 7009.3
S6XIPCH-1E = IPCH-15E+H 5.79E+14 0.0 50564.3
IPCH-15E+H = S4XIPCH-15E+H2 3.52E+14 0.0 6674.4
IPCH-15E+H = S3XIPCH-15E+H2 3.61E+14 0.0 6350.3
S4XIPCH-15E = A1IP+H 1.72E+14 0.0 30390.3
S3XIPCH-15E = A1IP+H 1.24E+14 0.0 30322.7
A1IP+H = PXA1IP+H2 9.31E+14 0.0 13611.3
PXA1IP = A1-+C3H6 1.14E+15 0.0 40940.3
PXA1IP = A1C2H3+CH3 6.33E+14 0.0 32466.9
IPCH-2E+H = T1XIPCH-2E+H2 1.33E+14 0.0 5993.2
T1XIPCH-2E = IPCH-15E+H 1.81E+14 0.0 48074.3
IPCH-3E+H = S2XIPCH-3E+H2 1.20E+14 0.0 7417.4
S2XIPCH-3E = IPCH-13E+H 1.35E+14 0.0 49221.0
S2XIPCH-3E = cC6H8-13E+iC3H7 5.49E+14 0.0 39370.4
IPCH-13E+H = S5XIPCH-13E+H2 4.85E+14 0.0 10420.5
IPCH-13E+H = S6XIPCH-13E+H2 2.88E+14 0.0 6558.0

S5XIPCH-13E = A1IP+H 1.94E+14 0.0 30296.9

S6XIPCH-13E = A1IP+H 1.74E+14 0.0 30225.3

! additional reactions

C4H7-1E3M+H = SAXC4H7+CH4 1.71E+14 0.0 35590.8 !IPCH+H = SXC2H4cC6H11+CH rxn

P4XC4H6-2E2M+H = C4H7-2E2M 1.33E+13 0.0 3260.7 ! =(C3H6+H=nC3H7) TS5 600 cm-1 USC Mech V2.0 !iC4H8+H(+M) = iC4H9(+M)

C4H7-2E2M+H = CH3CCHCH3+CH4 1.71E+14 0.0 35590.8 !IPCH+H = SXC2H4cC6H11+CH4 rxn

P4XC4H83M = C3H6+C2H5 2.57E+14 0.0 31562.7 ! P8XC8H14-1E7M = C3H6+P6XC6H11-1E

S2XC4H83M = CH3+C4H8-2 5.02E+13 0.0 31473.3 !S6XC8H14-1E7M = CH3+C8H14-16E

S3XC5H102M = C5H10-2E+CH3 5.02E+13 0.0 31473.3 !S6XC8H14-1E7M = CH3+C8H14-16E

S3XC5H102M = C4H7-1E3M+CH3 5.02E+13 0.0 31473.3 !S6XC8H14-1E7M = CH3+C8H14-16E

S3XC5H8-1E4M = CH3+C5H8-13E 5.02E+13 0.0 31473.3 !S6XC8H14-1E7M = CH3+C8H14-16E

P5XC5H8-2E2M = C2H4+CH3CCHCH3 1.89E+14 0.0 38619.2 !S4XC8H14-1E7M = C2H3+C6H11-1E5M

P1XCH2C4H6-1E3M = aC3H4+iC3H7 2.20E+13 0.0 24969.2 !S4XC6H10-1E3IP = C6H10-13E+iC3H7

P1XC5H8-2E4M+H = C5H9-2E4M 1.33E+13 0.00 3260.7 ! =(C3H6+H=nC3H7) TS5 600 cm-1 USC Mech V2.0 !iC4H8+H(+M) = iC4H9(+M)

C5H7-13E4M+H = T4XC5H7-13E+CH4 1.71E+14 0.0 35590.8 !IPCH+H = SXC2H4cC6H11+CH4 rxn

C5H9-1E4M+H = S4XC5H9-1E+CH4 1.71E+14 0.0 35590.8 !IPCH+H = SXC2H4cC6H11+C rxn

C5H9-2E4M+H = S4XC5H9-2E+CH4 1.71E+14 0.0 35590.8 !IPCH+H = SXC2H4cC6H11+C rxn

C4H6-1E23M = CH3CCH2+iC3H7 1.33E+14 0.0 63602.3 !C8H15-1E7M = aC3H5+P1XC5H104M

C4H6-1E23M = C3H6+C3H6 8.0E+05 1.81 53454 ! ! C5H9-1E4M = C3H6+C3H6

PLOG / 0.039 8.0E+05 1.81 53454/ ! 1.62E+06 /20 EST

PLOG / 1 1.62E+06 1.81 53454/ ! 08/TSAwip JetSurF 2.0

C4H5-13E2IP = iC4H5+iC3H7 1.33E+14 0.0 63602.3 !C8H15-1E7M = aC3H5+P1XC5H104

C4H7-1E2IP = C4H7-2+iC3H7 1.33E+14 0.0 63602.3 !C8H15-1E7M = aC3H5+P1XC5H104

C6H9-14E5M = aC3H5+iC4H7-1 1.33E+14 0.0 63602.3 !C8H15-1E7M = aC3H5+P1XC5H10

P4XC4H6-1E2IP = C2H4+T2XC4H6-1E3M 1.89E+14 0.0 38619.2 !S4XC8H14-1E7M = C2H3+C6H11-1E5M

T2XC4H6-1E3M+H = C4H7-1E3M 1.33E+13 0.0 3260.7 ! =(C3H6+H=nC3H7) TS5 600 cm-1 USC Mech V2.0 !iC4H8+H(+M) = iC4H9(+M)

P4XC4H6-1E3IP = C4H6+iC3H7 2.20E+13 0.0 24969.2 !S4XC6H10-1E3IP = C6H10-13E+iC3H7

P6XC6H10-2E2M = C2H4+P4XC4H6-2E2M 3.42E+14 0.0 30662.5 ! P8XC8H14-2E2M = C2H4+P6XC6H10-2E2M

S4XC6H10-1E5M = C2H3+C4H7-1E3M 1.89E+14 0.0 38619.2 !S4XC8H14-1E7M = C2H3+C6H11-1E5M

C5H7-14E2IP = aC3H5+T2XC4H6-1E3M 1.33E+14 0.0 63602.3 !C8H15-1E7M = aC3H5+P1XC5H104M

C5H7-13E3C3H7 = C3H6+C5H8-13E 4.95E+12 0.0 55419.0 !C8H15-1E7M = C3H6+C5H9-1E4M

P4XC4H6-2E2M = C4H5-13E2M+H 1.27E+24 -4.75 23777 ! Ref to C4H7 = C4H6+H

PLOG / 0.033 1.27E+24 -4.75 23777/

PLOG / 0.066 1.38E+26 -5.221 25729/

PLOG / 0.132 1.75E+28 -5.709 27764/

PLOG / 0.197 3.16E+29 -6.003 28985/

PLOG / 0.263 2.69E+30 -6.222 29890/

PLOG / 1.0 2.48E+53 -12.30 52000/

PLOG / 10 1.85E+48 -10.50 51770/

C8H14-16E = C3H6+C5H8-13E 3.97E+12 0.0 53586.8 !C6H11-1E3IP = C3H6+C5H9-2E4M

C4H7-1E3M = C2H4+C3H6 3.97E+12 0.0 53586.8 !C6H11-1E3IP = C3H6+C5H9-2E4M

END

3.5.3 Experimental Data

Verious experimental paremeter.

Mole fraction of various products and reactant after pyrolysis.

Table 3.8: Dwell time, pressure, temperature and initial concentration of IPCH used in the shock tube experiment.

SL No	**Dwell Time** (ms)	**Pressure** (P_5) bar	**Temperature** (T_5) K	**Initial concentration** $[IPCH]_0$
1	1.40	18.40	1345	0.005292282
2	1.53	20.19	1526	0.001040054
3	1.4	16.49	1282	0.002770585
4	1.45	13.53	1137	0.005299357
5	1.39	16.54	1228	0.005586043
6	1.39	15.72	1207	0.004284574
7	1.51	21.53	1565	0.002012414
8	1.54	21.23	1591	0.002399918
9	1.49	18.96	1318	0.00396227
10	1.48	21.84	1470	0.002504407
11	1.55	22.4	1505	0.002257313
12	1.46	9.77	923	0.00305758
13	1.42	18.31	1394	0.002136272
14	1.42	10.86	1092	0.003852127
15	1.42	15.49	1119	0.007809806
16	1.42	14.32	1128	0.007128833
17	1.45	17.62	1299	0.003978217
18	1.4	12.74	1050	0.006611676
19	1.51	18.88	1414	0.002493179
20	1.44	11.77	995	0.008088647
21	1.39	16.79	1197	0.008066803

Table 3.9: Mole fraction of various products and reactant

SL No	**Methane**	**Ethylene**	**Acetylene**	**Ethane**	**Propene**	**Propane**	**Allene**
1	0.00123	0.00321	0.00063	0.00031	0.00125	2.89E-05	4.92E-05
2	0.00071	0.00135	0.00116	0.00007	0.00011	0.00E+00	2.70E-05
3	0.00038	0.00096	0.00013	0.00011	0.00044	8.90E-06	1.36E-05
4	0.00007	0.00018	0.00002	0.00003	0.00011	0.00E+00	1.77E-06
5	0.00031	0.00076	0.00013	0.00010	0.00036	6.12E-06	1.15E-05
6	0.00020	0.00050	0.00006	0.00007	0.00028	3.97E-06	8.56E-06
7	0.00112	0.00222	0.00127	0.00016	0.00052	1.02E-05	2.94E-05
8	0.00137	0.00267	0.00147	0.00018	0.00064	1.69E-05	3.73E-05
9	0.00062	0.00145	0.00032	0.00015	0.00061	1.29E-05	2.35E-05
10	0.00104	0.00197	0.00101	0.00014	0.00059	1.63E-05	2.50E-05
11	0.00105	0.00204	0.00116	0.00014	0.00057	1.33E-05	2.64E-05
12	0.00000	0.00000	0.00000	0.00000	0.00000	0.00E+00	0.00E+00
13	0.00085	0.00189	0.00049	0.00019	0.00057	1.34E-05	3.14E-05
14	0.00003	0.00008	0.00001	0.00002	0.00005	0.00E+00	0.00E+00
15	0.00008	0.00023	0.00003	0.00004	0.00013	0.00E+00	3.67E-06
16	0.00009	0.00031	0.00004	0.00005	0.00015	0.00E+00	7.82E-06
17	0.00051	0.00133	0.00017	0.00015	0.00062	1.31E-05	1.77E-05
18	0.00002	0.00005	0.00000	0.00002	0.00003	0.00E+00	0.00E+00
19	0.00080	0.00188	0.00051	0.00016	0.00060	9.22E-06	2.60E-05
20	0.00000	0.00000	0.00000	0.00000	0.00000	0.00E+00	0.00E+00
21	0.00026	0.00078	0.00015	0.00011	0.00031	3.94E-06	1.18E-05

SL No	Propyne	Butene	Vinylacetylene	1,3-butadiene	1,3-butadiyne	2-butayne	1,3-butadiene,2-methyl
1	8.44E-05	1.43E-05	0.00016	0.00100	2.95E-05	7.48E-06	0.00E+00
2	5.88E-05	0.00E+00	0.00000	0.00014	0.00E+00	0.00E+00	0.00E+00
3	2.01E-05	6.68E-06	0.00005	0.00030	9.50E-06	0.00E+00	5.19E-06
4	4.65E-06	2.01E-06	0.00001	0.00006	1.90E-06	0.00E+00	0.00E+00
5	1.56E-05	2.11E-06	0.00004	0.00022	6.11E-06	1.82E-06	4.78E-06
6	8.46E-06	4.43E-06	0.00003	0.00016	8.18E-06	0.00E+00	2.33E-06
7	5.54E-05	8.87E-06	0.00005	0.00047	1.10E-05	2.55E-06	8.11E-06
8	7.01E-05	8.31E-06	0.00005	0.00054	1.59E-05	4.74E-06	8.67E-06
9	4.09E-05	6.44E-06	0.00005	0.00039	1.25E-05	4.45E-06	6.98E-06
10	4.79E-05	7.44E-06	0.00007	0.00046	1.75E-05	4.38E-06	1.04E-05
11	5.10E-05	5.63E-06	0.00006	0.00046	1.37E-05	3.20E-06	7.38E-06
12	0.00E+00	0.00E+00	0.00000	0.00000	0.00E+00	0.00E+00	0.00E+00
13	5.89E-05	5.63E-06	0.00007	0.00049	1.25E-05	2.85E-06	7.79E-06
14	0.00E+00	0.00E+00	0.00001	0.00002	0.00E+00	0.00E+00	0.00E+00
15	3.73E-06	0.00E+00	0.00001	0.00007	4.12E-06	0.00E+00	0.00E+00
16	5.60E-06	0.00E+00	0.00001	0.00010	5.18E-06	0.00E+00	0.00E+00
17	2.34E-05	6.44E-06	0.00007	0.00042	1.20E-05	1.96E-06	8.73E-06
18	0.00E+00	0.00E+00	0.00000	0.00002	0.00E+00	0.00E+00	0.00E+00
19	5.04E-05	9.25E-06	0.00007	0.00049	1.62E-05	4.98E-06	8.32E-06
20	0.00E+00	0.00E+00	0.00000	0.00000	0.00E+00	0.00E+00	0.00E+00
21	1.88E-05	2.01E-06	0.00003	0.00022	9.84E-06	5.34E-06	9.57E-06

SL No	**1-butyne**	**1,4-pentadiene**	**1,3-pentadiene**	**1,3-cyclopentadiene**	**1,4-pentadiene, 3-methyl**
1	7.78E-06	0.00017	2.36E-05	0.00012	1.13E-05
2	1.87E-05	0.00001	8.06E-06	0.00003	0.00E+00
3	0.00E+00	0.00006	1.64E-05	0.00003	4.07E-06
4	0.00E+00	0.00001	2.33E-06	0.00001	3.20E-06
5	0.00E+00	0.00004	1.28E-05	0.00002	4.62E-06
6	0.00E+00	0.00004	1.02E-05	0.00002	7.82E-06
7	1.57E-05	0.00005	1.77E-05	0.00008	4.80E-06
8	1.83E-05	0.00006	2.01E-05	0.00010	4.80E-06
9	1.78E-06	0.00008	1.83E-05	0.00004	8.33E-06
10	7.56E-06	0.00008	2.15E-05	0.00007	4.00E-06
11	1.04E-05	0.00007	1.91E-05	0.00007	4.48E-06
12	0.00E+00	0.00000	0.00E+00	0.00000	0.00E+00
13	6.82E-06	0.00009	2.25E-05	0.00007	3.52E-06
14	0.00E+00	0.00001	0.00E+00	0.00000	0.00E+00
15	0.00E+00	0.00001	5.43E-06	0.00001	0.00E+00
16	0.00E+00	0.00002	4.81E-06	0.00001	0.00E+00
17	0.00E+00	0.00009	2.06E-05	0.00005	6.66E-06
18	0.00E+00	0.00000	0.00E+00	0.00000	0.00E+00
19	3.56E-06	0.00008	2.14E-05	0.00007	4.16E-06
20	0.00E+00	0.00000	0.00E+00	0.00000	0.00E+00
21	2.34E-05	0.00003	1.00E-05	0.00002	4.64E-06

SL No	1,3-pentadiene,2-methyl	1,3-cyclopentadiene,5-methyl	1,3-cyclopentadiene,1-methyl	Benzene	1,3-cyclohexandiene
1	3.04E-05	5.56E-05	1.79E-05	0.00016	3.98E-05
2	0.00E+00	0.00E+00	0.00E+00	0.00013	0.00E+00
3	2.35E-05	2.28E-05	7.51E-06	0.00003	1.34E-05
4	1.60E-06	1.34E-05	7.75E-07	0.00001	3.05E-06
5	1.20E-05	1.82E-05	3.55E-06	0.00002	8.01E-06
6	1.01E-05	1.57E-05	3.10E-06	0.00001	6.73E-06
7	3.71E-06	1.80E-05	8.27E-06	0.00019	1.17E-05
8	3.81E-06	2.00E-05	7.93E-06	0.00023	1.27E-05
9	1.78E-05	2.94E-05	6.24E-06	0.00006	1.83E-05
10	1.02E-05	2.51E-05	9.95E-06	0.00014	1.79E-05
11	7.62E-06	2.16E-05	8.45E-06	0.00016	1.63E-05
12	0.00E+00	0.00E+00	0.00E+00	0.00000	0.00E+00
13	7.77E-06	8.74E-06	8.72E-06	0.00013	1.54E-05
14	0.00E+00	0.00E+00	0.00E+00	0.00000	0.00E+00
15	0.00E+00	6.20E-06	0.00E+00	0.00001	6.10E-06
16	3.20E-06	6.79E-06	0.00E+00	0.00001	4.88E-06
17	1.69E-05	2.89E-05	7.22E-06	0.00005	2.31E-05
18	0.00E+00	0.00E+00	0.00E+00	0.00000	0.00E+00
19	7.93E-06	2.56E-05	9.10E-06	0.00011	1.81E-05
20	0.00E+00	0.00E+00	0.00E+00	0.00000	0.00E+00
21	8.32E-06	1.38E-05	3.41E-06	0.00003	7.02E-06

SL No	**Cyclohexene**	**Toluene**	**Ethylidene-cyclohexane**	**Styrene**	**Isopropyl-cyclohexane**
1	0.00017	4.04E-05	0.00014	1.41E-05	0.00255
2	0.00000	2.02E-05	0.00000	1.90E-05	0.00010
3	0.00012	5.69E-06	0.00007	0.00E+00	0.00186
4	0.00005	0.00E+00	0.00003	0.00E+00	0.00508
5	0.00013	9.01E-06	0.00008	0.00E+00	0.00482
6	0.00012	6.56E-06	0.00006	0.00E+00	0.00372
7	0.00001	3.76E-05	0.00002	2.36E-05	0.00030
8	0.00002	4.37E-05	0.00002	2.32E-05	0.00037
9	0.00019	8.82E-06	0.00009	0.00E+00	0.00264
10	0.00006	2.28E-05	0.00005	1.17E-05	0.00087
11	0.00003	2.72E-05	0.00003	1.06E-05	0.00061
12	0.00000	0.00E+00	0.00000	0.00E+00	0.00306
13	0.00003	2.23E-05	0.00004	1.13E-05	0.00069
14	0.00002	0.00E+00	0.00000	0.00E+00	0.00378
15	0.00005	0.00E+00	0.00003	0.00E+00	0.00757
16	0.00005	0.00E+00	0.00003	0.00E+00	0.00683
17	0.00016	1.15E-05	0.00009	0.00E+00	0.00273
18	0.00002	0.00E+00	0.00002	0.00E+00	0.00654
19	0.00005	1.81E-05	0.00004	9.10E-06	0.00104
20	0.00000	0.00E+00	0.00000	0.00E+00	0.00809
21	0.00008	2.19E-06	0.00005	0.00E+00	0.00738

Chapter 4

1,3,5-trimethylcyclohexane pyrolysis at high pressure and temperature

4.1 Introduction

1,3,5-trimethylcyclohexane (C_9H_{18}) has the following properties: molar mass of 126.24 gm/mol, boiling point of 413 K, and density of 0.8±0.1 gm/cm^3. Like cyclohexane, it has several conformers: chair, half-chair, twist-boat, and boat; and most stable conformer is the chair conformer. Chair conformer also can exist in cis-chair and trans-chair conformer for 1,3,5-trimethylcyclohexane unlike cyclohexane. In cis-chair conformer, three CH_3 groups of 1,3,5-trimethylcyclohexane are present in equatorial position, while in trans conformer, two CH_3 groups are present in equatorial positions where the 3rd CH_3 group is present in axial position. The energy difference between cis-conformer (T135CH) and trans-conformer (T135CH-t) is only 1.8 kcal/mol (CBS-QB3 level of theory). Conformational inversion-topomerization process of cyclohexane[1], dimethylcyclohexane[2] are well known. However, no such study available for trimethylcyclohexane. Conformational inversion-topomerization process of trimethylcyclohexane follows the same path as that of cyclohexane and dimethylcyclohexane. Figure 4.1 shows the isomerization of cis to trans conformer of 1,3,5-trimethylcyclohexane. Chair and twist-boat conformer correspond to minima. Half-chair conformer is actually is a transition state (TS) between chair and twist-boat conformer whereas as boat conformer is a TS between two twist-boat conformers.

As discussed in the section 1.4, most of the previous studies of cyclo-alkanes have focused on cyclohexane and methylcyclohexane. Various experimental studies are found in the literature regarding oxidation, pyrolysis, flame and ignition (table

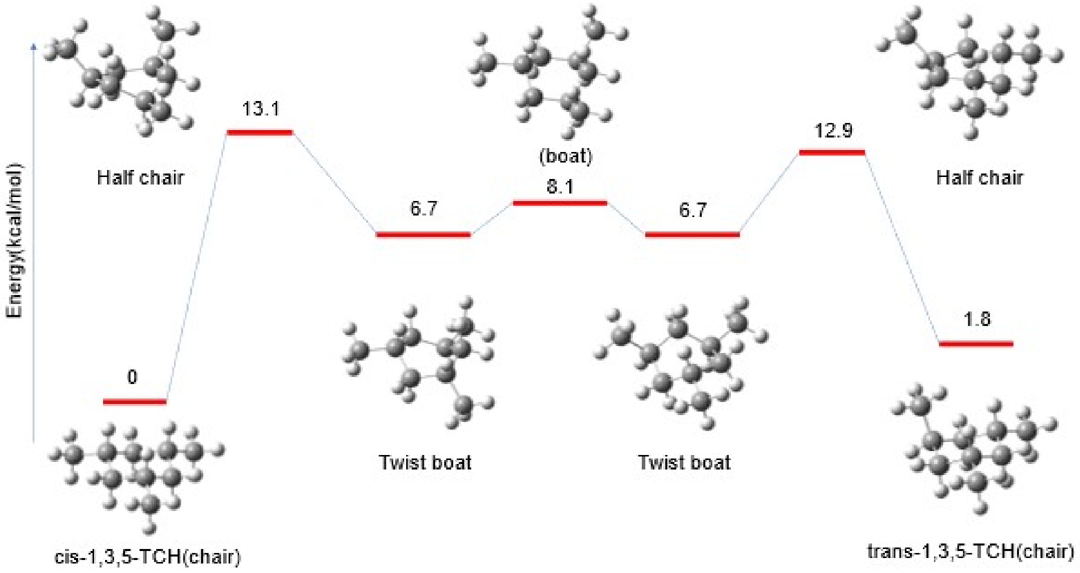

Figure 4.1: Conformational inversion-topomerization of 1,3,5-trimethylcyclohexane at CBS-QB3 level of theory.

1.9) of methylcyclohexane at different temperature and pressure regions. However, studies on alkylcyclohexane with multiple side-chains are quite limited. Few experimental studies available regarding pyrolysis, oxidation, ignition, and isomerization of dimethylcyclohexane (DCH) at different temperature and pressure (table 1.9). Only a couple of experimental studies of trimethylcyclohexane are published till date and both of which focussed only on 1,2,4-trimethylcyclohexane (table 1.9). On the other hand, theoretical studies on multiple side-chain alkylcyclohexane are even less (table 1.9). There is no theoretical study available till date for thermal decomposition of trimethylcyclohexane. Jia-Qi et al.[3] proposed surrogates of RP-3 after analysis of its composition and found 1,3,5-trimethylcyclohexane as one of the components. Recently Jin et al.[4] did a pyrolytic experiment on the surrogate mixture of three components comprising of n-dodecane (66.2%), 1,3,5-trimethylcyclohexane (18.0%) and n-propylbenzene (15.8%). However, there is so far no experimental or theoretical study available in the literature of pure 1,3,5-trimethylcyclohexane. The scarcity of experimental, theoretical, and kinetic modelling data on pyrolysis of trimethycyclohexane so far motivated us to do a detailed theoretical and experimental study on the pyrolysis of trimethylcyclohexane and then build its corresponding kinetic model. As 1,3,5-trimethylcyclohexane (135TCH) is proposed as a surrogate of RP-3, we have chosen this system (135TCH) in the current study. In this work, we report results from a detailed theoretical investigation of thermal decomposition of 135TCH using high level of quantum chemical calculation.

TST/VTST calculations have been used to obtain reliable rate constants for all important elementary reactions associated with 1,3,5-trimethylcyclohexane pyrolysis. These results have been used for detailed kinetic simulation of product profiles at various temperatures for comparison with shock tube experimental results.

4.2 Computational Details, Experimental Details and Kinetic Model

4.2.1 Geometry optimization and frequency calculation

The initial ring-opening path of 135TCH is associated with unstable biradical intermediate, and the decomposition path involve C-C bond lengthening during the bond dissociation (figure 4.3). To calculate the accurate energy barrier for these steps, one needs the multireference method as involved biradical possesses multireference characteristics. Geometry optimizations and frequency calculation for biradicals have been carried out using CASSCF method with the basis set of 6-31+g(d,p). For reaction associated with biradical intermediate, active space of six electrons occupying six orbitals (i.e., CAS(6e,6o) have been considered. A minimum active space (i.e.,CAS(2e,2o) has been chosen for CH_3 loss reaction channels. Single-point energies have been corrected using the MRCI method with the same active space and basis set. The zero-point energy (ZPE) scaling factor for the CASSCF method is 0.93[5]. For all other types of reaction single reference method has been used. Here we have been using CBS-QB3 method (section 2.2.1.1). IRC calculations were done with the same method to confirm that transition state connect with the reactant(s) and product(s). All multireference calculations have been performed using Molpro 2018 program while Gaussian 16 program has been used for CBS-QB3 calculation.

4.2.2 Reaction rate calculation

We calculated high-pressure limit rate in this as described in section 2.2.3.1.

Kinetic parameters A, E_a to be used in chemical kinetic modeling, have been obtained by fitting the calculated rate constant over the 800-2000 K temperature range to Arrhenius expression.

$$k(T) = A\exp(-E_a/RT)$$

As we are getting good fitting with temperature coefficient, n=0 in our considered temperature range, the temperature co-efficient has been taken as zero. All the rate calculations have been performed using the multiwell 2020 program.

4.2.3 Experimental Details

The high temperature thermal decomposition of 135TCH in argon bath has been carried out in the single pulse chemical shock tube (CST-1) facility available in our lab which is described details in the section 2.1.2. 135TCH used in the experiment has been procured from from TCI (Tokyo Chemical Industry) and is of >98% purity. Its exists in both cis (T135CH) and trans (T135CH-t) form. T135CH is 84% and T135CH-t is 16% in our reactant (as obtained from GC-FID analysis). 0.2 ml 135TCH (vapour pressure: 7 Torr) has been consistently taken for each experiment using a micropipette.

4.2.4 Kinetic Model

Detailed kinetic modelling for methylcyclohexane pyrolysis and combustion has been used as the base mechanism for the proposed 135TCH kinetic model[6]. For the sub-mechanism for 135TCH pyrolysis, rate parameters have been taken from theoretical calculation. The present kinetic model includes 302 species and 967 reactions. The thermodynamic parameters for the new species found in 135TCH mechanism have been calculated in this work as thermodynamic data for many of the dehydrogenation intermediates from 135TCH are not available. Their frequencies and standard entropies have been calculated at CBS-QB3 method. Their standard enthalpies of formation have been calculated using atomization energy (section 2.2.2).

The formulae, nomenclature, and structure of those species have all been given in the supporting information. The pyrolysis simulation has been performed with the normal reflected shock code whereas the sensitivity analysis have been conducted using the close homogeneous batch reactor code in CHEMKIN software.

4.3 Results and Discussion

In the present work, we have studied the thermal decomposition of both cis (T135CH) and trans (T135CH-t) conformers of 1,3,5-trimethylcyclohexane so as to also understand the impact of conformational structures on thermal decomposition. The thermal decomposition of 1,3,5-trimethylcyclohexane can be classified into six classes of reactions as:

i) Unimolecular decomposition and isomerization of 135TCH
ii) H-abstraction reaction by H atom and CH_3 radical
iii) Dissociation of alkene and alkyl-cyclohexene
iv) Decomposition and isomerization of alkyl-cyclohexane radicals
v) Decomposition and isomerization of alkenyl radicals

vi) Stepwise dehydrogenation of cyclic intermediate.

The global scheme of thermal decomposition of 135TCH is shown in figure 4.2.

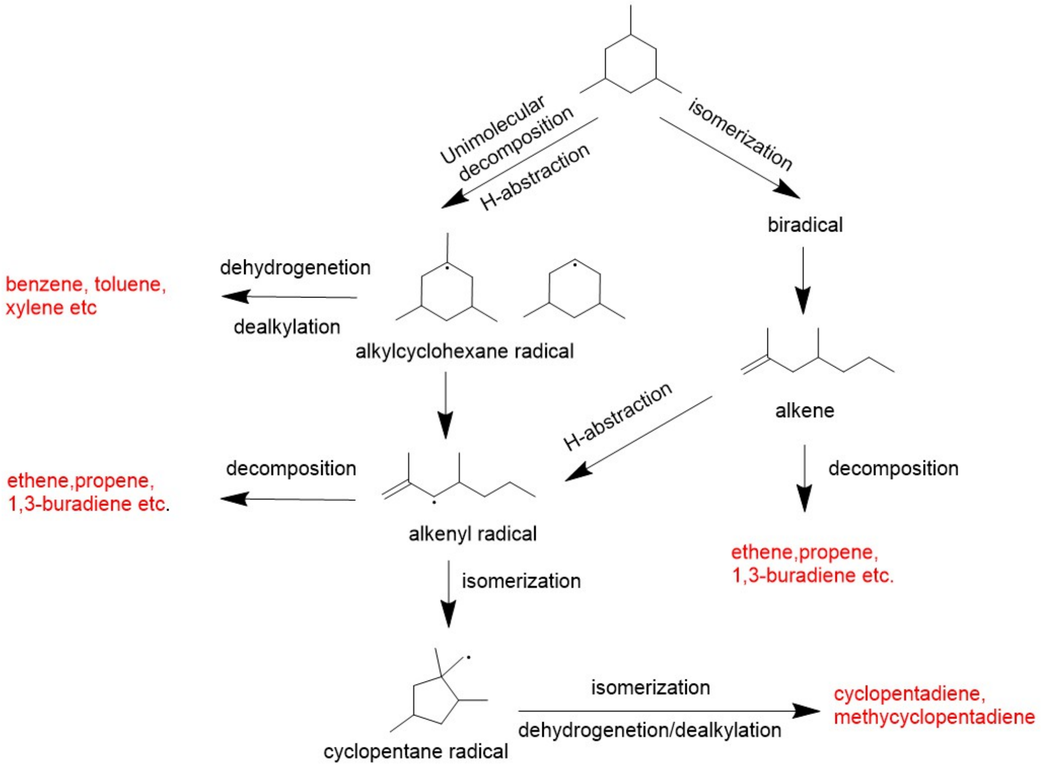

Figure 4.2: Global reaction scheme of 135TCH decomposition.

The initial reaction involves the C-C bond dissociation from side-chain CH_3 group to form dimethyl-cyclohexane radical as well as ring opening of cyclohexane group to form three types of dimethylheptene (alkene) via a biradical intermediate. Then chain reaction occurs through the H-abstraction from different C atoms within 135TCH by H atom and CH_3 radical. The H-abstraction reactions results in formation of different trimethylcyclohexane radicals which can further either isomerize to form alkenyl radical or form cyclic intermediate/aromatic by sidewise dehydrogenation/dealkylation. Alkenes, alkenyl radicals decompose into small molecules and radicals (secondary reactions). In the following sections, we have first discussed the potential energy surface (PES) and analyzed the reaction mechanism of all kinds of reaction classes mentioned above. Thereafter, the rate parameters associated with each of the reactions involved have been discussed further. After that we will discuss experimental results and simulations.

4.3.1 Potential energy surface and analysis of reaction mechanism

4.3.1.1 Unimolecular decomposition and isomerization of 135TCH

All the possible reaction channels of the initial decomposition and isomerization pathways of both cis (T135CH) and trans (T135TH-t) conformer are shown below in figure 4.3. For T135CH, only one unique CH_3 group is present (equatorial position) whereas for T135CH-t two different CH_3 group present (two equatorial and one axial).

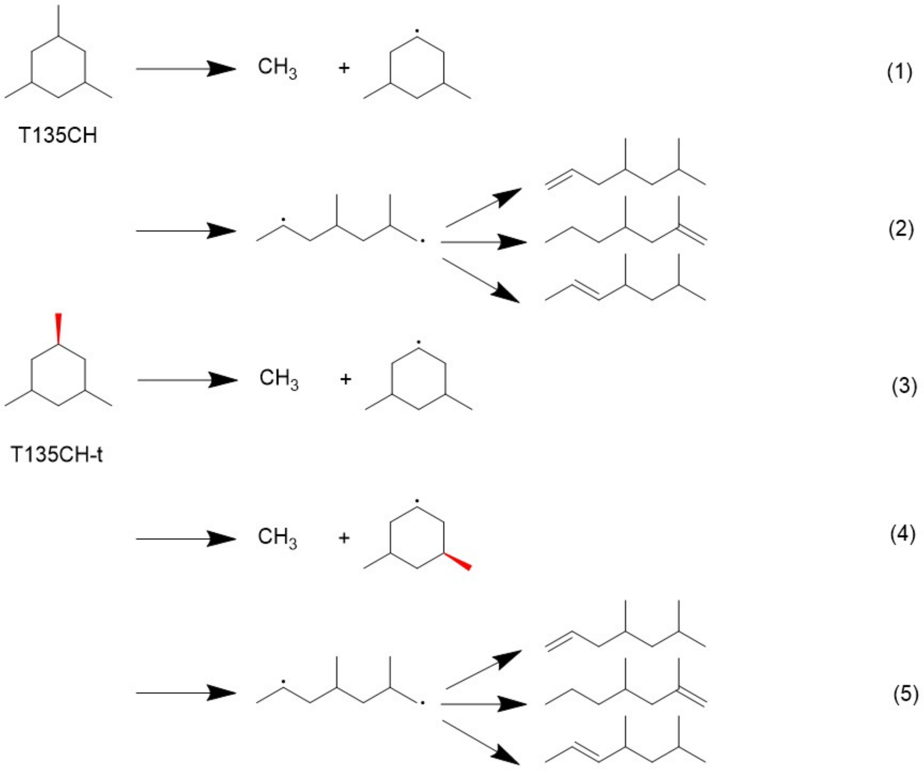

Figure 4.3: Decomposition and isomerization of 135TCH. Red bonds indicate CH_3 group at axial position.

Side-chain CH_3 in T135CH dissociation leading to CH_3 radical and cis-dimethylcyclohexyl radical (channel 1). On the other hand, dissociation of side-chain CH_3 in T135CH-t leads to CH_3 radical and both cis and trans dimethylcyclohexyl radicals (channel 3 and 4). T13CH has only one unique ring C-C bond. So, isomerization process occurs via only one biradical intermediate followed by intramolecular H-migration (channel 2). For T135CH-t, we have considered C-C bond dissociation adjacent to axial CH_3 group which leads to same biradical intermediate. Side-chain CH_3

dissociation of 135TCH is a barrier-less process and its potential energy surface (PES) has been obtained by relaxed scan along with the C-C bond with 0.1 Å step size. Figure 4.4 shows PES of the initial decomposition and isomerization of T135CH at MRCI//CAS(6,6)/6-31+g(d,p) (red colour) and CAS(6,6)/6-31+g(d,p) (black colour) level of theory for isomerization channel (channel 2) and that at MRCI//CAS(2,2)/6-31+g(d,p) (red colour) and CAS(2,2)/6-31+g(d,p) (black colour) level of theory for decomposition channel (channel 1).

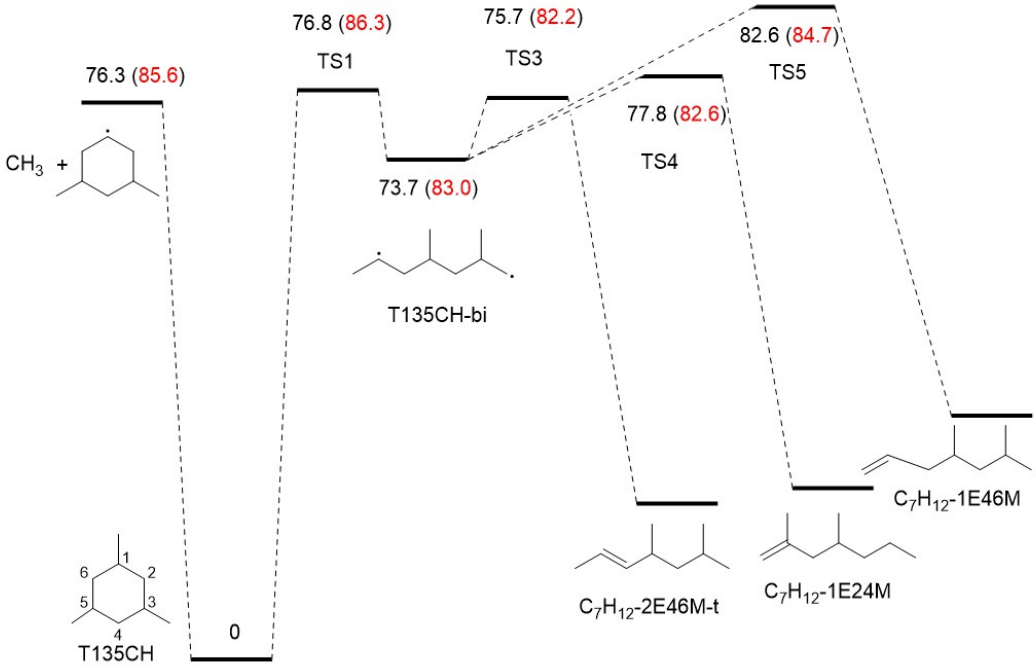

Figure 4.4: PES for initial decomposition and ring opening isomerization of T135CH. For decomposition, the methods were MRCI/6-31+g(d,p)//CAS(2,2)/ 6-31+g(d,p) (value in the bracket with red colure) and CAS(2,2)/ 6-31+g(d,p) (value with black colour). For isomerization, the methods were MRCI/6-31+g(d,p)//CAS(6,6)/ 6-31+g(d,p) (value in the bracket with red colure) and CAS(6,6)/ 6-31+g(d,p) (value with black colour). Energy unit: kcal/mol.

Figure 4.5 shows the PES of the initial decomposition of T135CH-t. The PES shows that for T135CH, initial decomposition and isomerization are very closely energetic process and energy difference is below 1 kcal/mol (MRCI level of theory). For T135CH-t, dissociation of axial CH_3 group is more energetically favourable than dissociation of equatorial CH_3 group. For T135CH-t, initial decomposition is favourable than ring opening isomerization process with the energy difference more than 2 kcal/mol. Isomerization happens via two steps. In the first step, the cyclohexane ring-opens with C-C bond dissociation and forms a biradical. In the

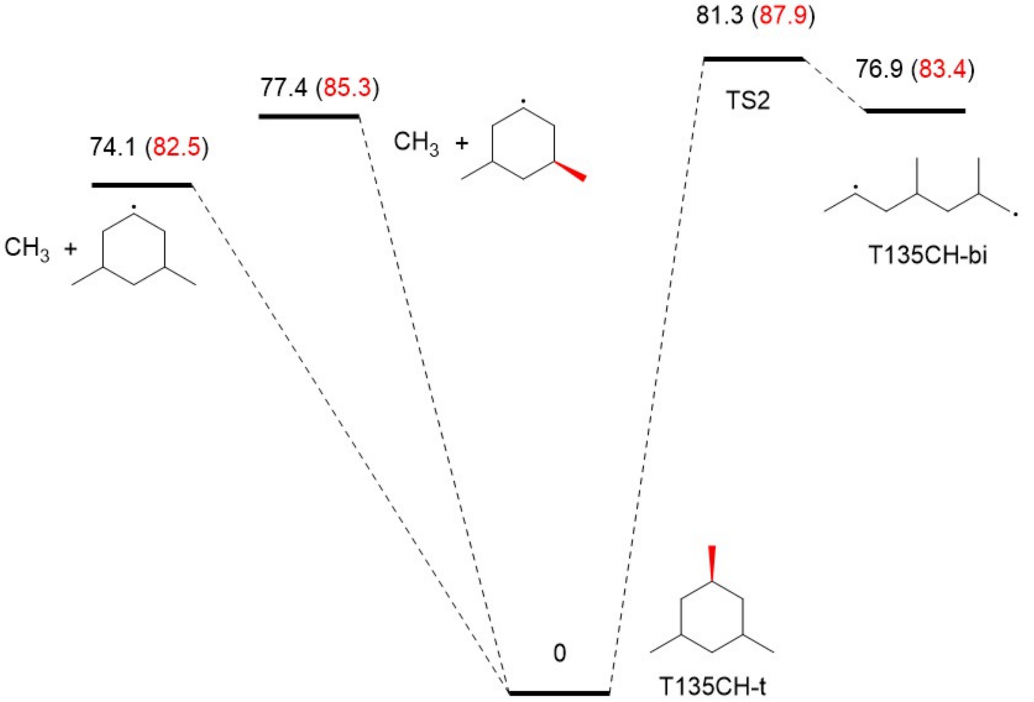

Figure 4.5: PES for initial decomposition of T135CH-t. The methods were MRCI/6-31+g(d,p)//CAS(2,2)/ 6-31+g(d,p) (value in the bracket with red colure) and CAS(2,2)/ 6-31+g(d,p) (value with black colour). Energy unit: kcal/mol.

next step, H-migration happens, and an alkene is formed. T135CH leads to biradical intermediate via TS1 whereas T135CH-t leads to the same biradical via TS2. Energy barrier associated with TS2 is higher than that for TS1. H-migration from biradical intermediate to form alkene involves either a 6-membered cyclic transition state (TS) or an 8-membered cyclic TS and the former is energetically more favorable than the later one. H-migration from T135CH-bi (biradical intermediate) leads to three dimethylheptene isomers ($C_7H_{12} - 2E46M - t$, $C_7H_{12} - 1E24M$, and $C_7H_{12} - 1E46M$). Formation of $C_7H_{12} - 1E46M$ happens via TS5 (an 8-membered cyclic TS). The energy barrier for this process is much higher than the energy barrier for the formation of $C_7H_{12}-2E46M-t$ and $C_7H_{12}-1E24M$, which happen via TS3 and TS4, respectively (6-membered cyclic TS). To understand the effect multi side-chain CH_3 groups in the initial decomposition and isomerization of trimethylcyclohexane as well as the impact of conformational structures on initial decomposition and isomerization, in Table 4.1, we compare the energy barriers of T135CH and T135CH-t with methylcyclohexane[5] data.

We can see that barrier for CH_3 elimination from equatorial position is similar for T135CH and T135CH-t, whereas axial CH_3 elimination is energetically

Table 4.1: Comparison of relative energy of initial decomposition and isomerization channel of methyl-cyclohexane, T135CH, and T135CH-t. Energy unit: kcal/mol. Method: MRCI

	methylcyclohexane[5]	T135CH	T135CH-t
CH_3 elimination channel	84.0	85.6	82.5(axial)/ 85.3(equatorial)
TS of C1-C2 ring opening	85.0	86.3	87.9
TS of C2-C3 ring opening	89.0	-	-
TS of C3-C4 ring opening	89.0	-	-

favourable by around 3 kcal/mol for the later. The barrier for CH_3 elimination of methylcyclohexane (MCH) is in between the barriers for equatorial and axial elimination reactions in T135CH-t. Energy barrier for ring-opening of T135CH is less than that of T135CH-t although the difference is less than 1 kcal/mol. Except the ring opening at C1-C2 bond, energy barrier for ring opening of methylcyclohexane is higher than T135CH and T135CH-t and the energy difference with T135CH is 2.7 kcal/mol and with T135CH-t is 1.1 kcal/mol. Ring opening at C1-C2 bond is energetically favourable for MCH and the energy difference with that of T135CH is 1.3 kcal/mol and with T135CH-t is 2.9 kcal/mol.

4.3.1.2 H-abstraction reaction by H atom and CH_3 radical

Except for unimolecular decomposition and isomerization of 135TCH, we have used CBS- QB3 level of theory for all other classes of reactions. Figure 4.6 shows PES for H-abstraction reaction of T135CH by H-atom/CH_3 radical. T135CH has three different carbon atoms, hence three trimethylcyclohexane radicals are formed by abstraction reaction. Figure 4.7 and figure 4.8 shows PES for H-abstraction reaction of T135CH-t by H-atom and CH_3 radical respectively. T135CH-t has six different carbon atoms, so such six trimethylcyclohexane radicals formed by abstraction reaction. The energy barrier for these type of reactions (abstractions) is low although energy barrier for abstraction by H atom is less compared to that by CH_3 radical. It follows the order: H-abstraction at the primary carbon >H-abstraction at the secondary carbon>H-abstraction at the tertiary carbon.

In Table 4.2 Comparison of energy barrier of H-abstraction reaction by H atom between methylcyclohexane, T135CH and T135CH-t. Between T135CH and T135CH-t, we can see the energy barriers are only different for the abstraction on the carbon centre near the axial CH_3 group (C1(H) abstraction, C2(H) abstraction and C3(H) abstraction) whereas no effect on the far from axial CH_3 group

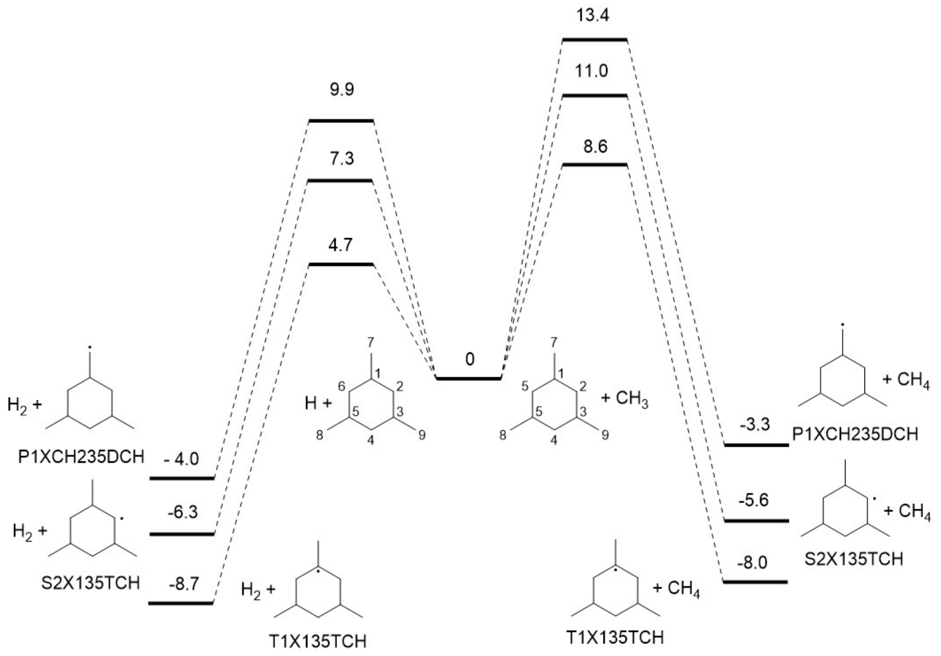

Figure 4.6: Potential energy surface for H-atom abstraction reactions of T135CH by H atom and CH_3 radical. Energy unit: kcal/mol.

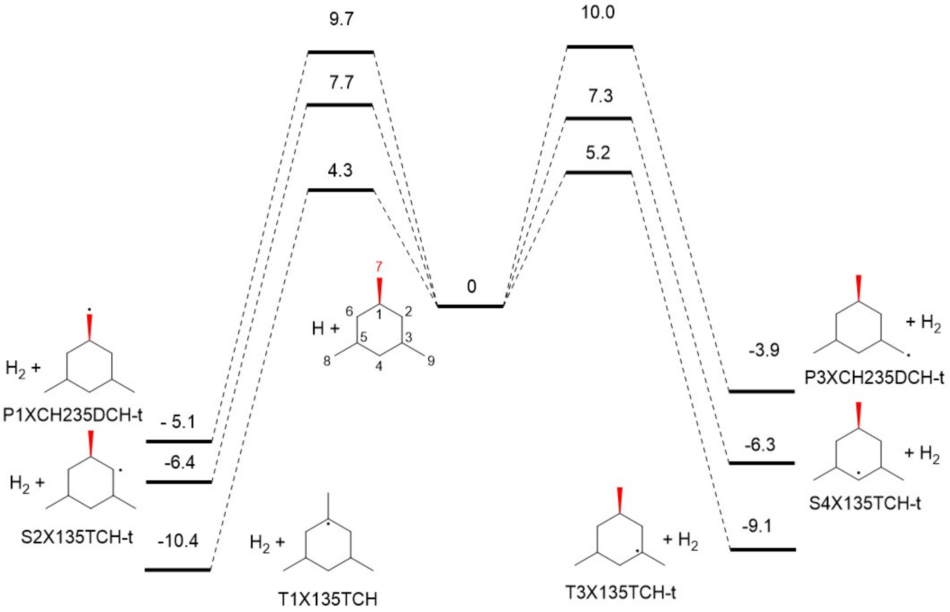

Figure 4.7: Potential energy surface for H-atom abstraction reactions of T135CH-t by H atom. Energy unit: kcal/mol.

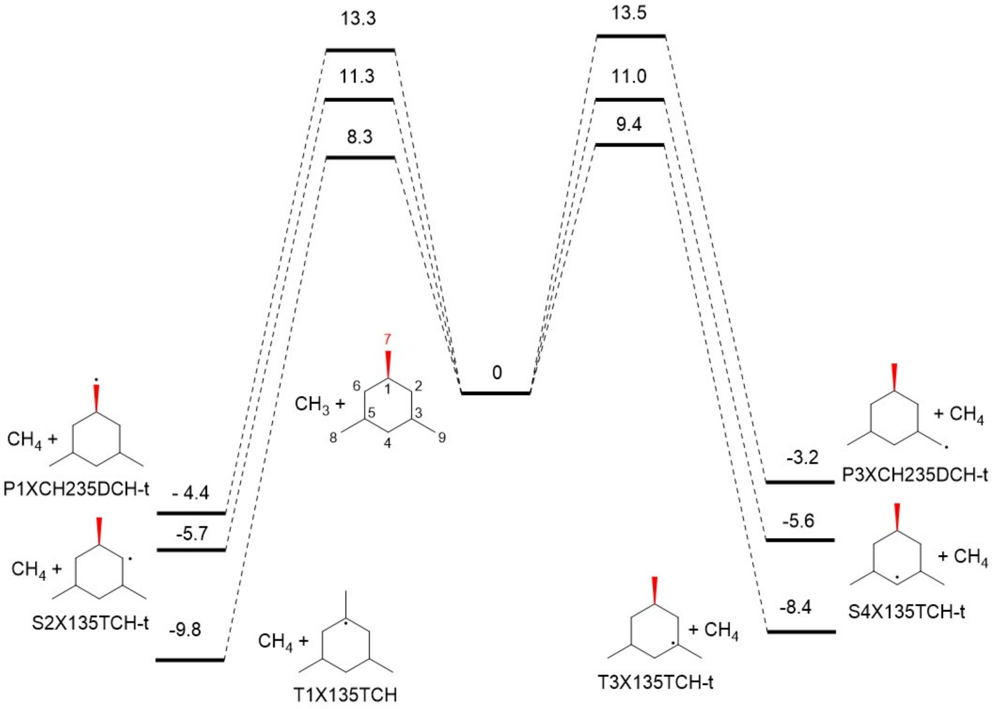

Figure 4.8: Potential energy surface for H-atom abstraction reactions of T135CH-t by CH_3 radical. Energy unit: kcal/mol.

(C4(H) abstraction). However, the corresponding energy difference is very small and is found to be within 0.5 kcal/mol. Between MCH and T135CH, the barrier is same for abstraction at primary and secondary carbon centres but little different for abstraction at tertiary carbon centre (0.2 kcal/mol less for T135CH).

Table 4.2: Comparison of energy barrier of H-abstraction reaction by H atom between methylcyclohexane(MCH), T135CH and T135CH-t. Energy unit: kcal/mol. Method: CBS-QB3.

	MCH[6]	T135CH	T135CH-t
Primary carbon H-abstraction	9.9	9.9	9.7(equatorial) /10.0(axial)
C1(H) abstraction	4.9	4.7	4.3
C2(H) abstraction	7.3	7.3	7.7
C3(H) abstraction	7.2	-	5.2
C4(H) abstraction	7.2	-	7.3

4.3.1.3 Decomposition and isomerization of dimethylcyclohexane radical and trimethylcyclohexane radicals

Unimolecular decomposition of 135TCH leads to both cis and trans dimethylcyclohexane (figure 4.4 ,figure 4.5) while H-abstraction reaction leads to various trimethylcyclohexane radicals (Figure 4.6 and figure 4.7). These radicals can further undergo either dissociation (H/CH_3 elimination) or isomerization. Figure 4.9, figure 4.10, figure 4.11, and figure 4.12 show PESs of all the reactions.

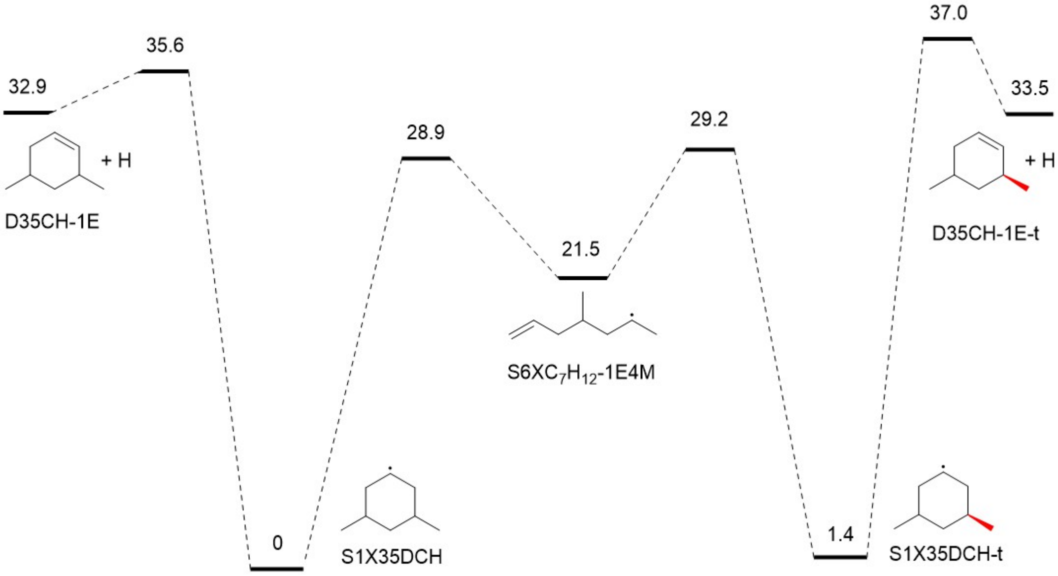

Figure 4.9: Isomerization and decomposition reactions of cis and trans dimethylcyclohexane radicals (S1X35DCH and S1X35DCH-t)). Energy unit: kcal/mol.

It is evident from the figure that dissociation occurs via either $\beta - C - C$ scission or $\beta - C - H$ scission and while isomerization takes place via $\beta - C - C$ scission to open the six-membered ring. The energy barrier for the isomerization process is lower than those of other pathways for cis and trans dimethylcyclohexane radicals (S1X35DCH and S1X35DCH-t) and cis-trimethylcyclohexane radicals ($P1XCH_2 35DCH$, S2X135TCH, and T1X135TCH), which is similar to methylcyclohexane radical. For methylcyclohexane radical, ring-opening isomerization process always has the lowest barrier[6]. However, this is not true for all trimethylcyclohexane radicals. For S2X135TCH-t, dissociation via $\beta - C - C$ scission (i.e., CH_3 radical elimination from equatorial position) has the lowest barrier. CH_3 elimination by $\beta - C - C$ scission from equatorial position is energetically favourable than CH_3 elimination from axial position although the energy difference is only 0.9 kcal/mol. The energy barrier of dissociation via $\beta - C - H$ scission is 1-5 kcal/mol higher than $\beta - C - C$ scission. Primary trimethylcyclohexane radical

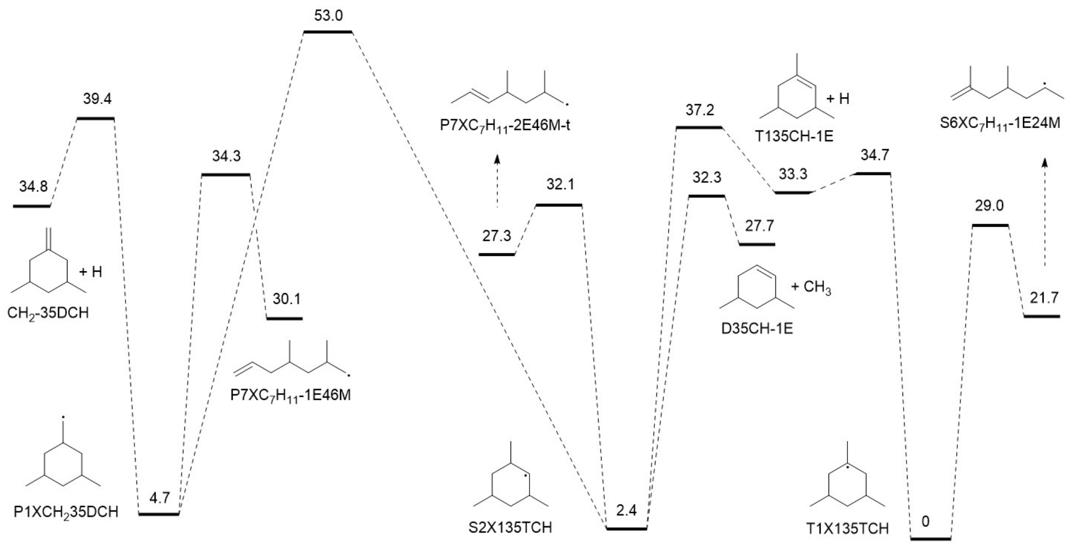

Figure 4.10: Isomerization and decomposition reactions of cis trimethylcyclohexane radicals (P1XCH235DCH, S2X135TCH, and T1X135TCH). Energy unit: kcal/mol.

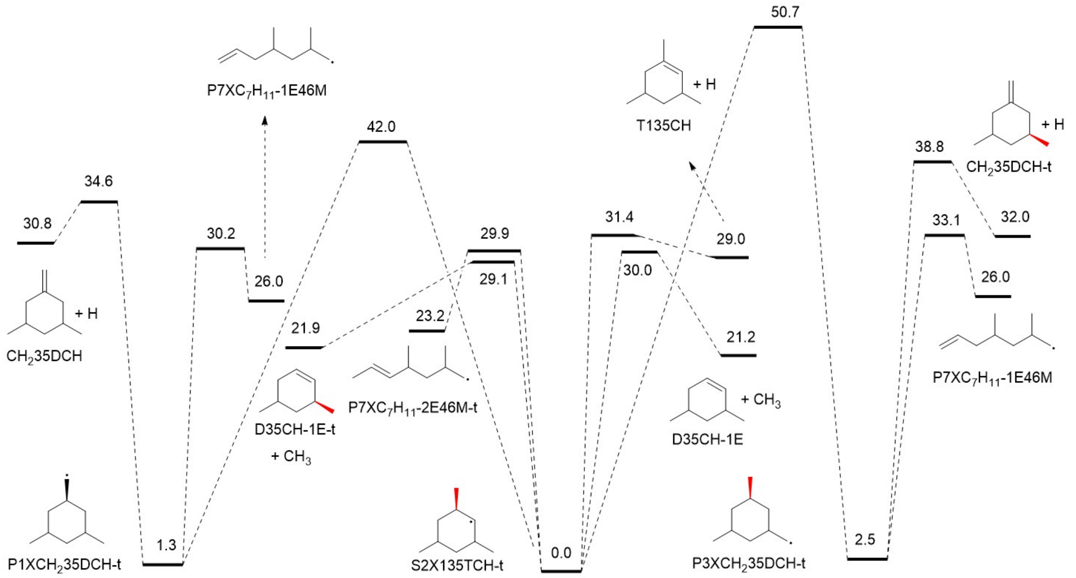

Figure 4.11: Isomerization and decomposition reactions of trans trimethylcyclohexane radicals (P1XCH235DCH-t, S2X135TCH-t, and P3XCH235DCH-t). Energy unit: kcal/mol.

to secondary trimethylcyclohexane radical isomerization occurs via intra molecular H-migration associated with high energy barrier and the energy barrier for

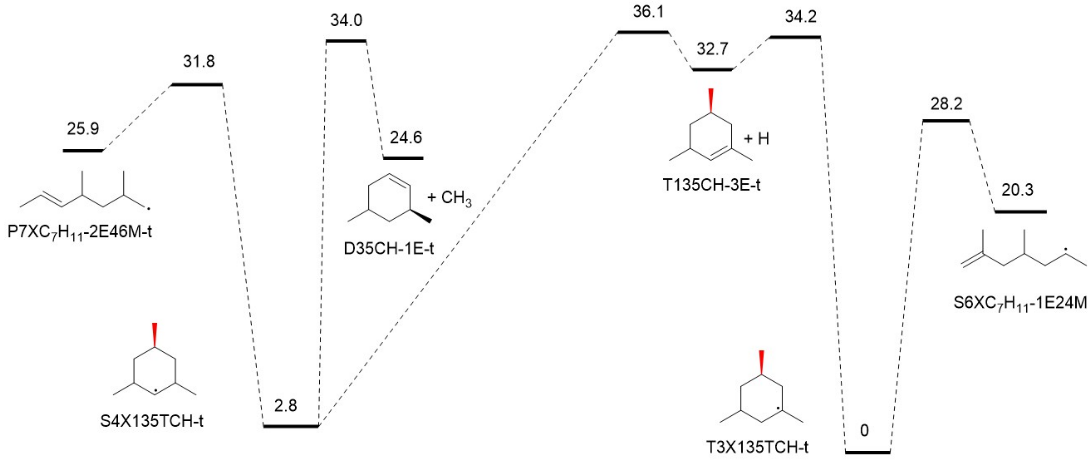

Figure 4.12: Isomerization and decomposition reactions of trans trimethylcyclohexane radicals (S4X135TCH-t, and T3X135TCH-t). Energy unit: kcal/mol.

cis-isomer is 48.3 kcal/mol (i.e. $P1XCH_2 35DCH$ to S2X135TCH isomerization). For trans-isomer the H-migration can happen from both CH_3 group at axial and equatorial positions.

Table 4.3: Comparison between ring-opening isomerization of methylcyclohexane radical and trimethylcyclohexane radical. Energy unit: kcal/mol. MCH-methylcyclohexane; C2 and C3 carbon radical centre of MCH has two paths for ring-opening isomerization.

Similar structure	MCH[6]	T135CH	T135CH-t
Primary carbon racial	28.6	29.6	28.9 (CH_2 at axial position)/ 30.6 (CH_2 at equatorial position)
Tertiary carbon radical centre	29.6	29.0	28.2
Secondary carbon radical centre (C2 carbon radical centre)	28.9/29.5	29.7	29.9
Secondary carbon radical centre (C3 carbon radical centre)	28.7/29.7	-	-
Secondary carbon radical centre (C4 carbon radical centre)	30.2	-	31.8

Energy barrier associated with H-migration at axial CH_3 group is 40.7 kcal/mol

($P1XCH_2 35DCH - t$ to S2X135TCH-t isomerization) while at equatorial CH_3 group is 48.2 kcal/mol (($P3XCH_2 35DCH - t$ to S2X135TCH-t isomerization). The energetics corresponding to ring opening isomerization path for cis-trimethylcyclohexane, trans-trimethylcyclohexane and methylcyclohexane radical have been compared in the table 4.3.

For primary cyclohexane radical of trans trimethylcyclohexane ($P1XCH_2DCH - t$ and $P3XCH_2DCH - t$), ring-opening adjacent to axial CH_2 is energetically favourable than equatorial CH_2. For primary and tertiary radical, ring-opening for trans-trimethylcyclohexane is energetically favourable whereas for secondary radical ring-opening for cis trimethylcyclohexane is energetically favourable although the energy difference is within 1 kcal/mol. Between MCH and trimethylcyclohexane (135TCH), for primary and secondary carbon radical centre, ring-opening for MCH is energetically favourable whereas for tertiary carbon radical centre, ring-opening for 135TCH is energetically favourable although the energy difference is within 1.5 kcal/mol.

Table 4.4: Lowest energy pathway comparison between MCH radicals, T135CH radicals, and T135CH-t radicals. Energy unit: kcal/mol.

	Bond dissociation	Energy barrier
MCH[6]	isomerization via $\beta - C - C$ scission	28.6
T135CH	isomerization via $\beta - C - C$ scission	29.0
T135CH-t	isomerization via $\beta - C - C$ scission	28.2

For all alkylcyclohexane radicals, isomerization via $\beta - C - C$ scission is the lowest energy channel. T135CH-t radical has the lowest barrier for a ring-opening channel and T135CH has the highest barrier for a ring-opening channel.

4.3.1.4 Dissociation of alkene and alkylcyclohexene

Alkenes which are formed by the initial isomerization process of 135TCH can further undergo decomposition. We have considered both H-abstraction and C-C dissociation reactions of alkenes. Liu et al.[7] carried out theoretical studies of C4-C6 alkenes and showed allylic H-abstraction as the most energetically favourable one. Hence, we have considered only the allylic H-abstraction reactions in this study. Also, Wang's[8] theoretical study revealed allylic C-C bond having the lowest dissociation energy. Thus, we have considered only the allylic C-C bond dissociation in this work. Figure 4.13 shows the PES of all the alkenes.

There are two types of C-C bond dissociation reaction for alkenes:

a) simple bond dissociation reaction (which does not have any saddle point and is a barrier-less reaction),

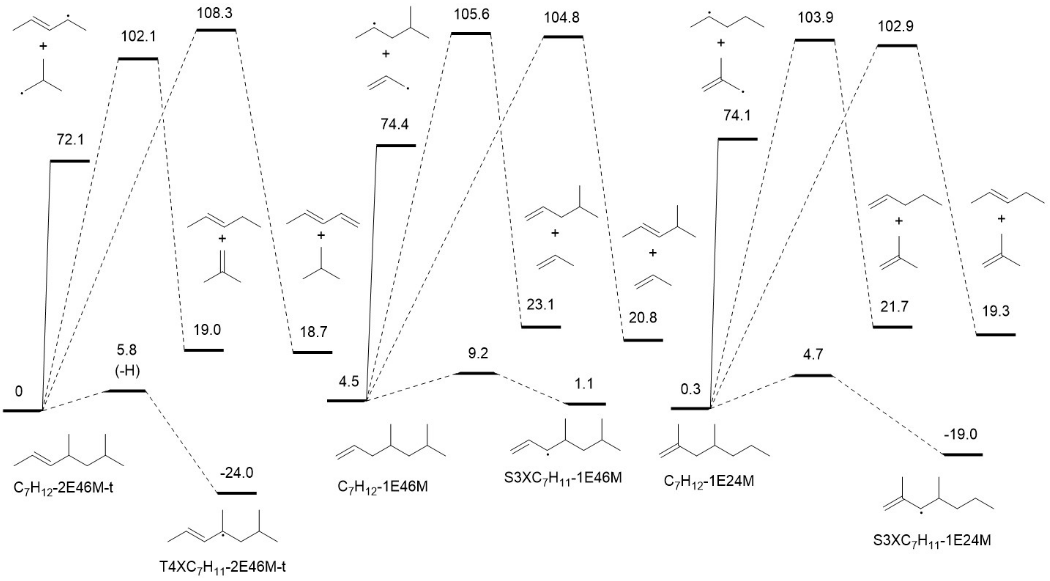

Figure 4.13: H-abstraction and decomposition reactions of $C_7H_{12}-2E46M-t$, $C_7H_{12}-1E46M$, and $C_7H_{12}-1E24M$. (-H) indicates H-abstraction reaction by H atom. The solid line indicates reaction without saddle point. Energy unit: kcal/mol.

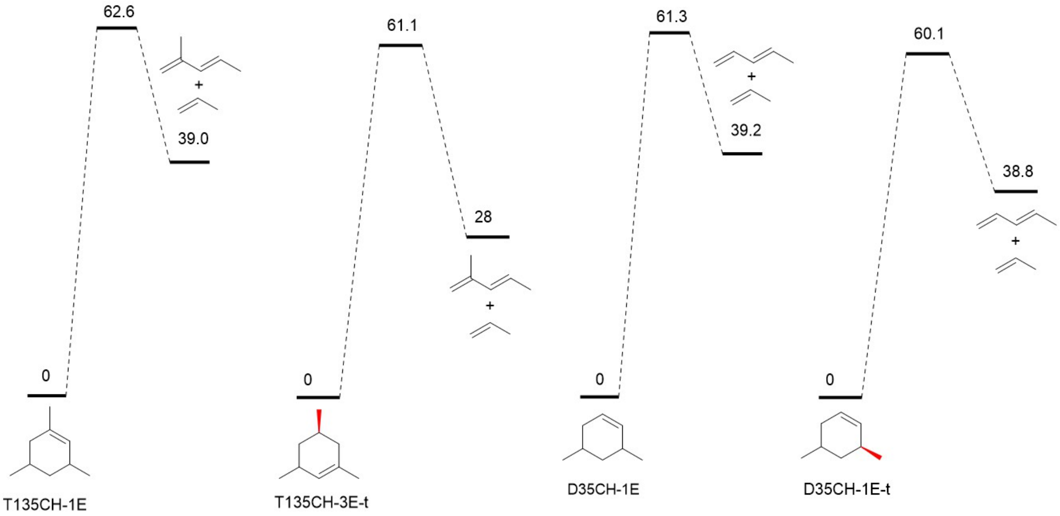

Figure 4.14: Reverse DA reaction for T135CH-1E, T135CH-3E-t, D35CH-1E and D35CH-1E-t. Energy unit: kcal/mol.

b) C-C bond dissociation followed by H-migration. C-C bond dissociation followed by H-migration are high energetic processes.

Simple C-C bond dissociation of $C_7H_{12}-1E46M$ has the lowest energy barrier among all the alkene. The energy barrier for C-C dissociation followed by H-migration is also lowest for $C_7H_{12}-1E46M$ among all the alkene.

Alkyl-cyclohexene is formed from the elimination reaction of Alkyl-cyclohexane radical. For D35CH-1E, T135CH-1E, D35CH-1E-t, and T135CH-3E-t we have considered reverse Diels-Alder reaction as a dissociation channel (figure 4.14). We can see that trans cyclohexene has the lower energy barrier for reverse Diels-Alder reaction. Dimethylcylohexene has lower energy barrier for DA reaction compared to trimethylcyclohexene. These alkylcyclohexene can also form cyclic intermediate by stepwise dehydrogenation, which is discussed later.

4.3.1.5 Decomposition and isomerization of alkenyl radicals

Different alkenyl radicals are formed by isomerization of alkyl-cyclohexane radicals via ring-opening. They are also formed by H-abstraction reaction of alkene. Here we will discuss all the possible pathways of decomposition of the alkenyl radicals. Alkenyl radical can undergo either $\beta-C-C$ scission to form small hydrocarbons, or it can isomerize to form cyclopentane intermediate (via ring-closing) or other alkenyl radicals (via intramolecular H-migration).

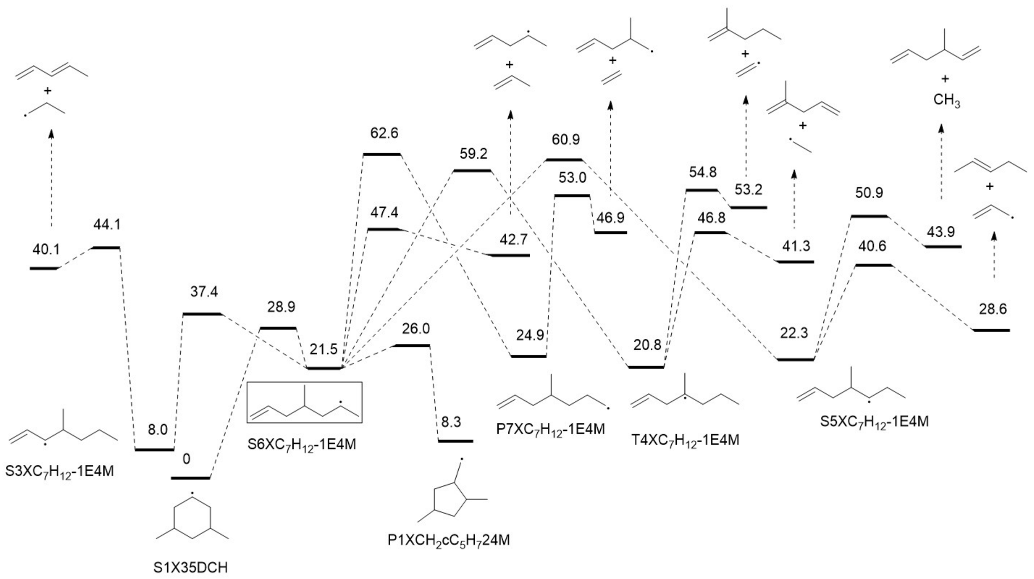

Figure 4.15: PES for decomposition reaction of $S6XC_7H_{12}-1E4M$. Energy unit: kcal/mol.

Figure 4.15, 4.16, 4.17 and 4.18 show all PES. We can see from all PES that isomerization to cyclopentene radical is the lowest energy pathways (except for $P7XC_7H_{11}-1E46M$ where cyclopentane radical formation is not possible).

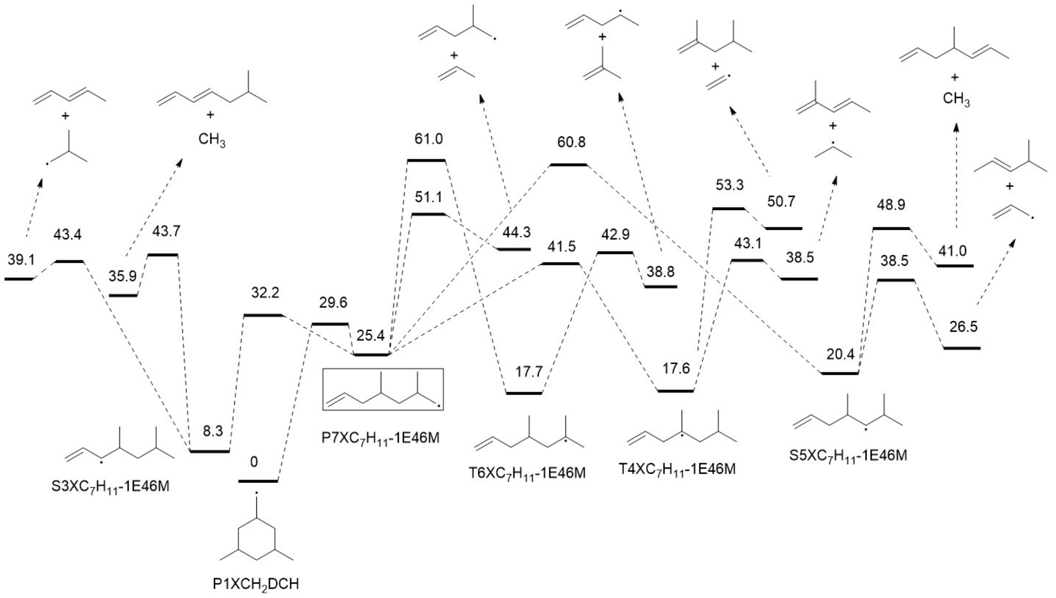

Figure 4.16: PES for decomposition reaction of $P7XC_7H_{11}-1E46M$. Energy unit: kcal/mol.

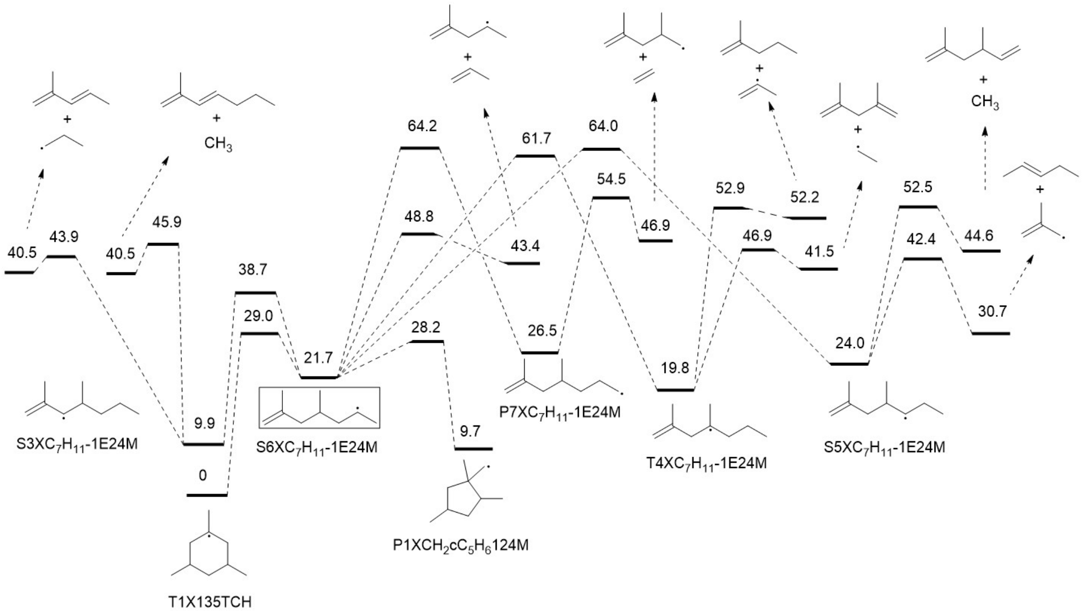

Figure 4.17: PES for decomposition reaction of $S6XC_7H_{11}-1E24M$. Energy unit: kcal/mol.

For isomerization process by intramolecular H-migration; 1,5-H shift (only for

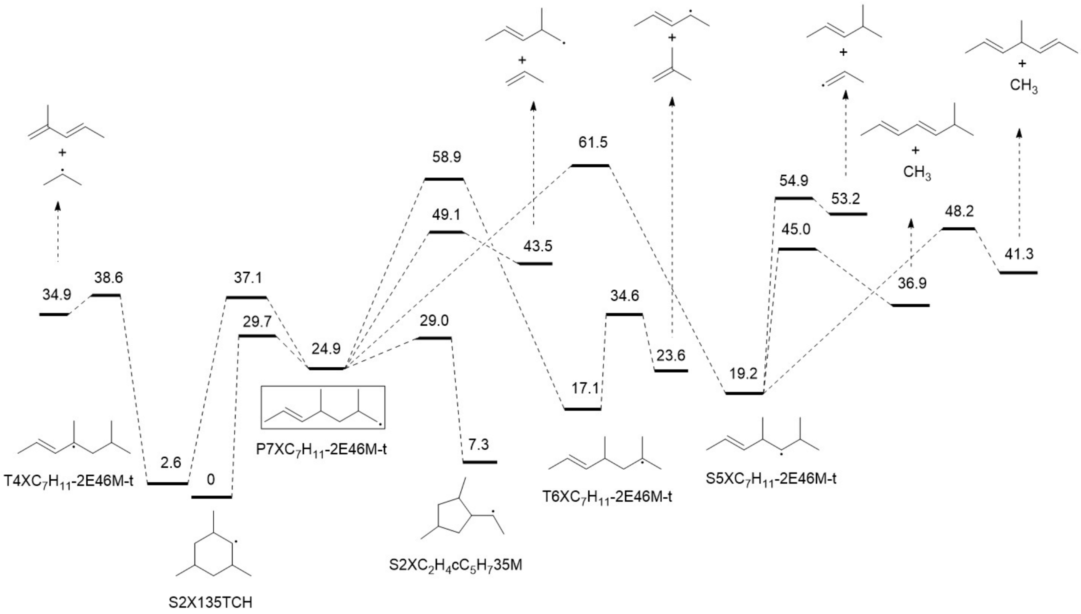

Figure 4.18: PES for decomposition reaction of $P7XC_7H_{11}-2E46M-t$. Energy unit: kcal/mol.

$P7XC_7H_{11}-1E46M$) and 1,4-H shift (for all other alkyl-radical) have lower energy barrier as these processes are associated with six-membered cyclic TS (for 1,5-H shift) and five-membered cyclic TS (for 1,4-H shift) respectively. $\beta-C-C$ scission of all the alkenyl radicals leads to several small hydrocarbons which include diene (butadiene, methyl-pentadiene, pentadiene, hexadiene etc.), alkene (ethylene, propene, butene ect.), alkyl-radical (CH_3, C_2H_5) etc.

Table 4.5: Comparison of energy barrier for isomerization pathways for all alkenyl radicals. Energy unit: kcal/mol.

	Isomerization to cyclopentane	1,4-H shift	1,5-H shift
$S6XC_7H_{12}-1E4M$	4.5	15.9	-
$P7XC_7H_{11}-1E46M$	-	17.1	6.8
$S6XC_7H_{11}-1E24M$	6.5	17	-
$P7XC_7H_{11}-2E46M-t$	4.1	12.2	-

4.3.1.6 Stepwise dehydrogenation of cyclic intermediate

Decomposition of alkylcyclopentane radicals

From the isomerization of the alkenyl radical, three different alkylcyclopentane radicals are formed.

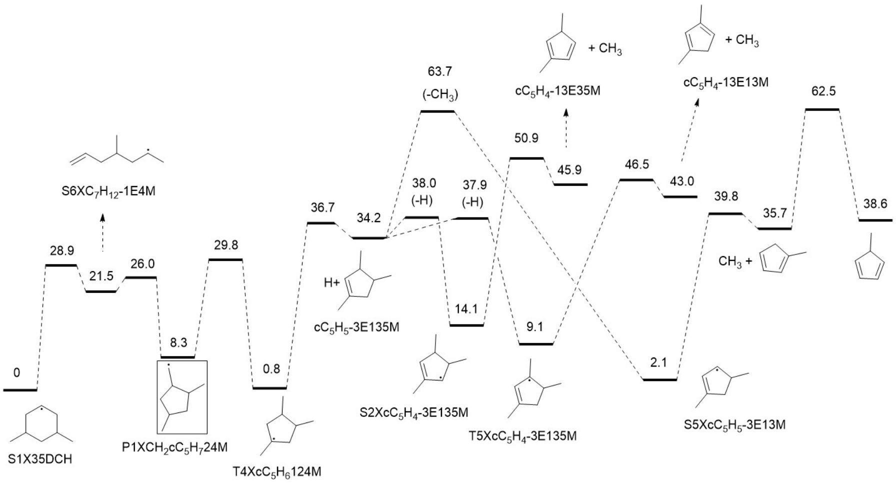

Figure 4.19: Stepwise decomposition of $P1XCH_2cC_5H_724M$. $(-CH_3)$ indicates CH_3-abstraction reaction by H atom and(-H) indicates H-abstraction reaction by H atom. Energy unit: kcal/mol.

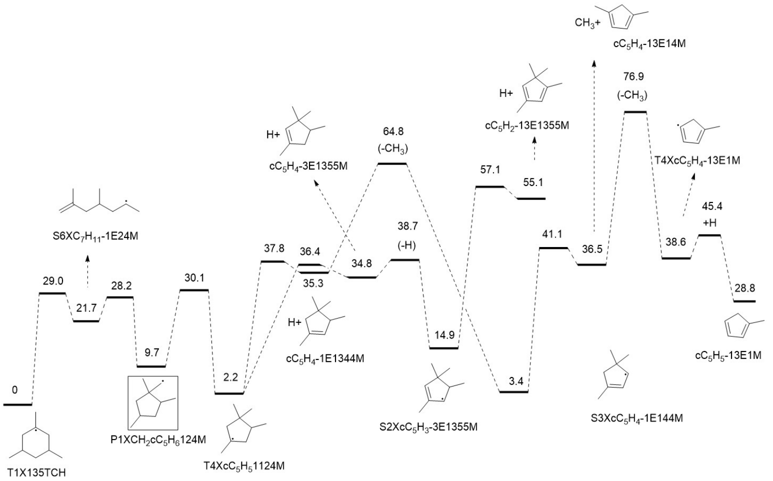

Figure 4.20: Stepwise decomposition of $P1XCH_2cC_5H_6124M$. $(-CH_3)$ indicates CH_3-abstraction reaction by H atom and(-H) indicates H-abstraction reaction by H atom. Energy unit: kcal/mol.

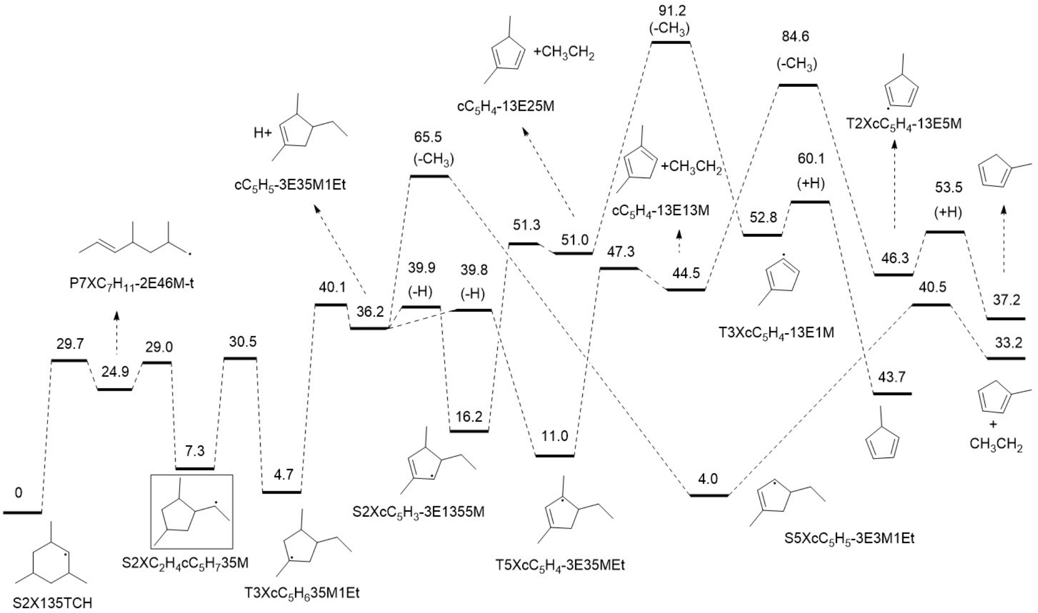

Figure 4.21: Stepwise decomposition of $P1XC_2H_4cC_5H_735M$. $(-CH_3)$ indicates CH_3-abstraction reaction by H atom and(-H) indicates H-abstraction reaction by H atom. Energy unit: kcal/mol.

Figure 4.19 figure 4.20 and figure 4.21 illustrate the decomposition of those alkylcyclopentane leading to cyclopentadiene and methylcyclopentadiene. All alkylcyclopentane radicals first undergo an intermolecular isomerization process to form more stable alkylcyclopentane radical through a five-membered ring TS. Then subsequent elimination, abstraction, elimination reaction happens, which leads to the formation of either cyclopentene or methylcyclopentene.

Dehydrogenation of alkylcyclohexene

Figure 4.22 and figure 4.23 show the PES of stepwise dehydrogenation of alkylcyclohexenes. Alkylcyclohexene forms allylic alkylcyclohexane radical by H-abstraction reaction. Both D35CH-1E and T135CH-1E can form either tertiary allylic alkylcyclohexane radical or secondary allylic alkylcyclohexane radical. Formation of tertiary allylic alkylcyclohexane radical is energetically favourable. These allylic cyclohexane radicals lead to alkylcyclohexadiene by either H-elimination (dehydrogenation) or CH_3 radical elimination (dealkylation). CH_3 radical elimination is energetically favourable than H atom elimination. Alkyl-cyclohexadiene then follows a similar pathway to form aromatic products.

Table 4.6 and table 4.7 shows the comparison of aromatisation process among D35CH-1E, T135CH-1E and cyclohexene. Table 4.6 shows the formation of aro-

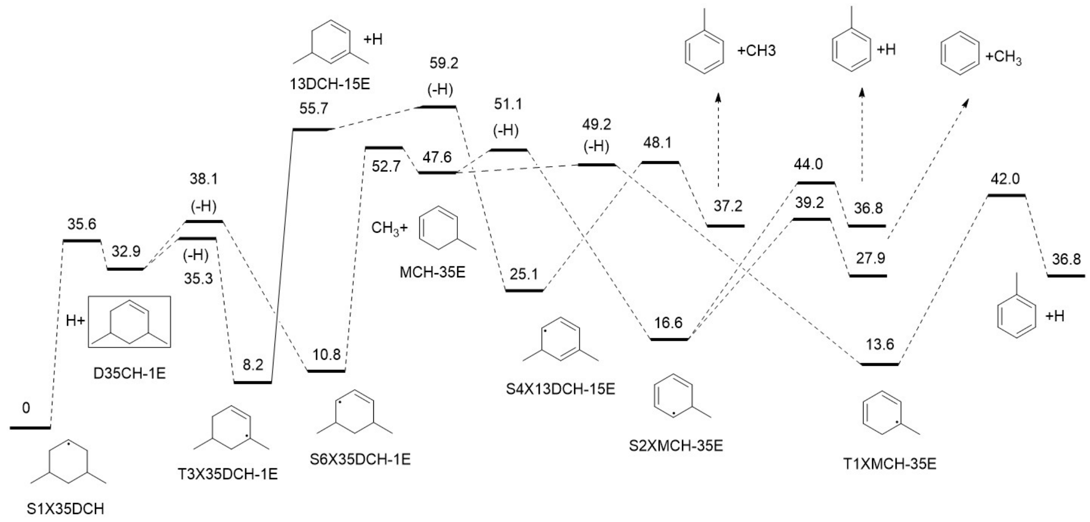

Figure 4.22: Stepwise decomposition of D35CH-1E. (-H) indicates H-abstraction reaction by H atom. Energy unit: kcal/mol.

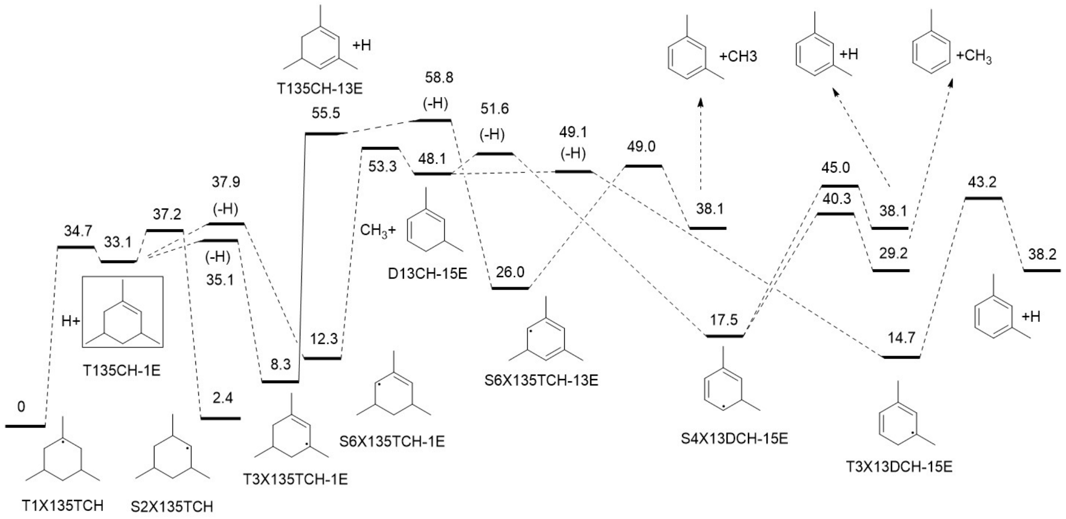

Figure 4.23: Stepwise decomposition of T135CH-1E. (-H) indicates H-abstraction reaction by H atom. Energy unit: kcal/mol.

matic intermediate via tertiary allylic alkylcyclohexane radical whereas table 4.7 shows formation of aromatic intermediate via secondary allylic alkylcyclohexane radical. From the table we can see for both D35CH-1E and T135CH-1E aromatic formation is energetically favourable than cyclohexene. Again, between D35CH-1E and T135CH-1E, aromatic formation is energetically favourable for T135CH-1E than D35CH-1E. These observations suggest that multi side-chain CH_3 substitution favours step-wise dehydrogenation/dealkylation.

Table 4.6: Comparison of energy barrier of stepwise dehydrogenation pathways between dimethylcyclohexene and trimethylcyclohexene via tertiary allylic cyclohexene radical with cyclohexene. Energy unit: kcal/mol.

	D35CH-1E	T135CH-1E	cyclohexene
H-abstraction to form cyclohexene radical	2.4	2	5.4
Elimination reaction to form cyclohexadiene	47.5	47.2	48.5
H-abstraction to form cyclohexadiene radical	3.5	3.3	3.4
Elimination reaction to form aromatic molecule	23.0 (CH_3 elimination)	23.0 (CH_3 elimination)	28.1

Table 4.7: Comparison of energy barrier of stepwise dehydrogenation pathways between dimethylcyclohexene and trimethylcyclohexene via secondary allylic cyclohexene radical with cyclohexene. Energy unit: kcal/mol.

	D35CH-1E	T135CH-1E	cyclohexene
H-abstraction to form cyclohexene radical	5.2	4.8	5.4
Elimination reaction to form cyclohexadiene	41.9	41.0	48.5
H-abstraction to form cyclohexadiene radical	1.6	1	3.4
Elimination reaction to form aromatic molecule	28.4	28.5	28.1

4.3.2 Rate Calculation

We calculate the high-pressure limit (HPL) rate for all the reactions using TST for the reaction with saddle point and VTST for the reaction without saddle point for the temperature range of 800-2000 K.

4.3.2.1 Unimolecular decomposition and isomerization of 135TCH

Unimolecular decomposition channel (i.e., CH_3 elimination channel) is a barrierless process. To get PES, we did stepwise optimization (relax scan figure 4.24) and then calculate rate parameters using VTST. Isomerization of 135TCH occurs through two steps (figure 4.4, figure 4.5) and we have calculated rate parameters for both steps. From figure 4.4, we can see that at MRCI method, in some cases, energy of TS of H-migration step (2nd step of isomerization process) is less than biradical intermediate (T135CH-bi). A similar situation was encountered for the isomerization process of methylcyclohexane[5] as well. Authors decided to increase the barrier artificially to ensure that the TS was above the product[5]. However, in our study, we took CASSCF energy barriers for 2nd step of the isomerization process as we wanted to avoid such artificial increase of barrier.

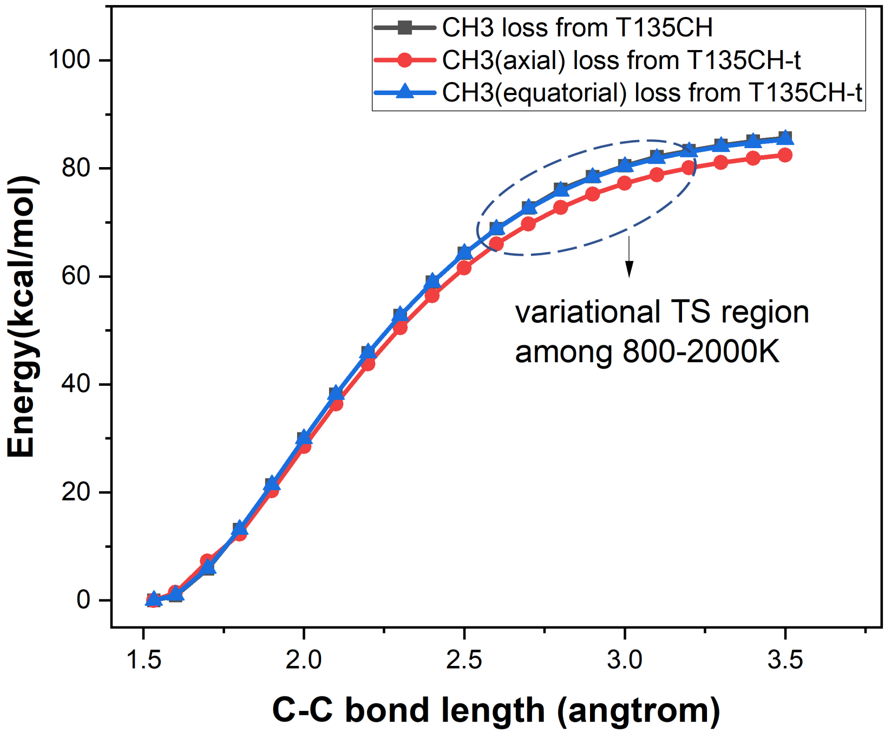

Figure 4.24: Stepwise optimized potential energy curve of 135TCH dissociation via CH_3 loss. Method: MRCI/6-31+g(d,p)//CAS(2,2)/ 6-31+g(d,p).

As figure 4.24 shows, the barrier height of the variational transition state varies for CH_3 loss channel of T135CH from 69.7-78.5 kcal/mol for CH_3(equatorial) elimination channel of T1135CH-t varies from 75.8-81.8 kcal/mol and that for CH_3(axial) loss channel of T1135CH-t comes around 61.6-77.2 kcal/mol within the studied temperature range. Comparing the energies of the variational transition state for the CH_3 eliminations channels with that of the isomerization channel (figure 4.4), one cannot neglect those channels. Axial CH_3 group elimination is the lowest energy process whereas as equatorial CH_3 group elimination from both T135CH and T135CH-t are very close in energy and are high energetic process compared to axial CH_3 elimination.

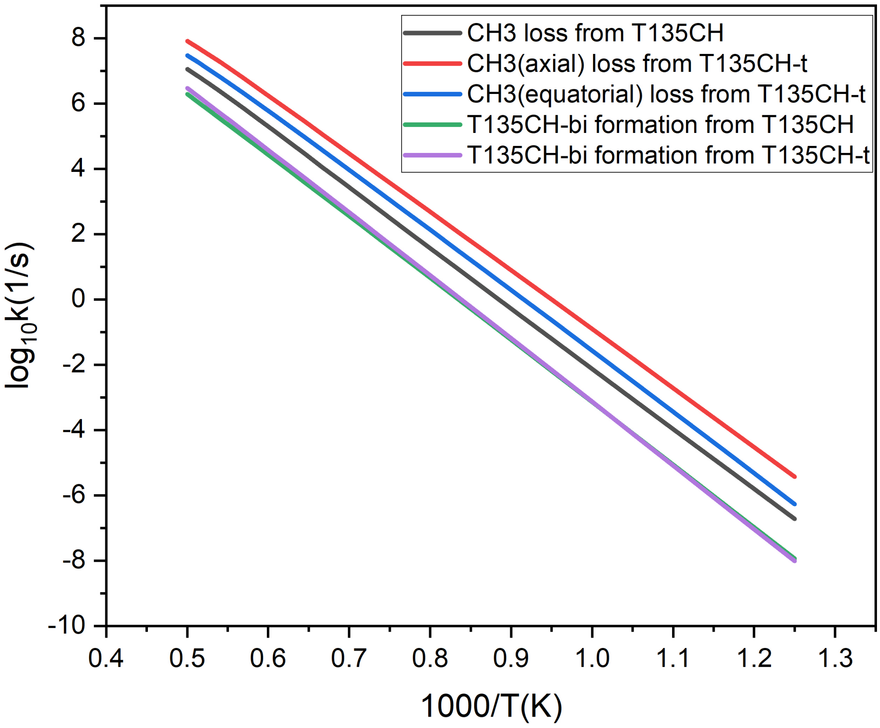

Figure 4.25: HPL rate constant for 135TCH decomposition and ring-opening step of isomerization (biradical formation).

From figure 4.25 and figure 4.26, we can see that, the rate constant of the ring-opening step (1st step) to form biradical is much lesser than the H-migration step (2nd step). This result follows the same trend as that of isomerization of methyl-cyclohexane as reported by Wang et al.[5]. The rate of H-migration reaction from T135CH-bi to form $C_7H_{12} - 1E46M$ (TS is an 8-membered cyclic ring associated

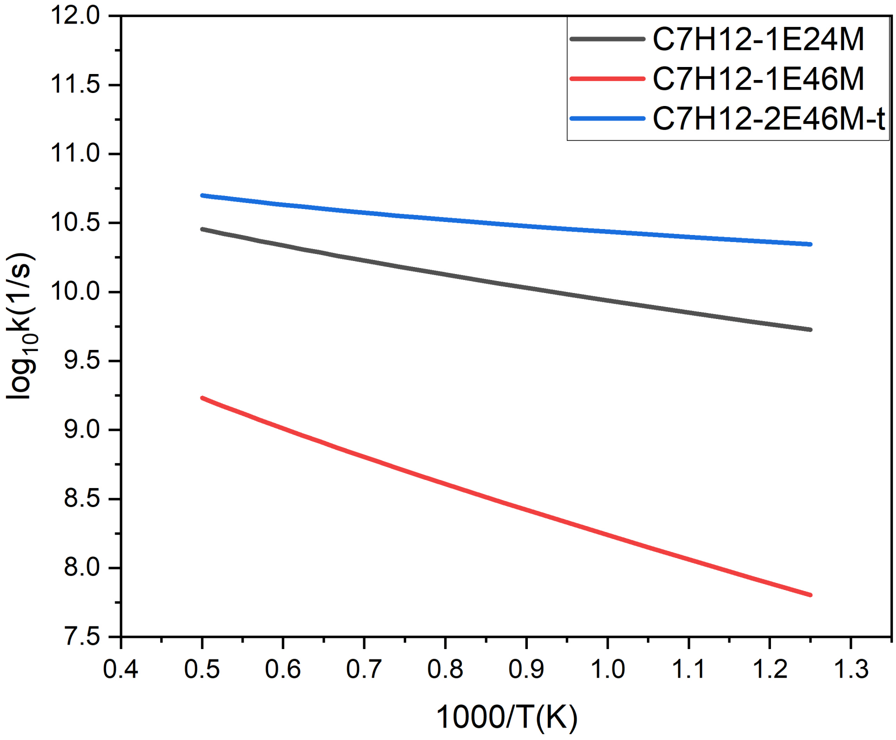

Figure 4.26: HPL rate constant for 2nd step of isomerization of 135TCH i.e., intramolecular H-migration from biradical to form alkene.

with high energy barrier) is lesser than that for the H-migration from T135CH-bi which leads to $C_7H_{12} - 2E46M - t$ and $C_7H_{12} - 1E24M$ (TS is a 6-membered cyclic ring). The unimolecular decomposition reactions dominate over isomerization reactions for both T135CH and T135CH-t. The dominant reaction channel is the axial CH_3 removal channel of T135CH-t followed by CH_3 removal channel of T135CH. The rate constants of ring-opening of both T135CH and T135CH-t are similar.

In figure 4.27 we can see that the rate constants of CH_3 removal from MCH is less than the rate of axial CH_3 removal of T135CH-t. However, the rate constants of CH_3 removal from T135CH as well as equatorial CH_3 removal from T135CH-t is comparatively less than the rate constants of CH_3 removal from MCH. In figure 4.28 we compare the rate of isomerization of MCH with rate of biradical formation of T135CH and T135CH-t. Rate constant of ring-opening process of T135CH and 135CH-t are found to be in between the value of the rate constant of three different

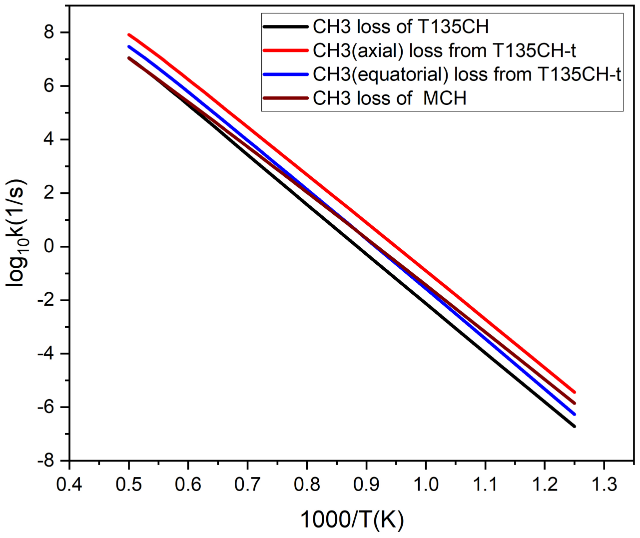

Figure 4.27: Comparison of the rate constant of the decomposition reaction of T135CH, T135CH-t, and MCH[5].

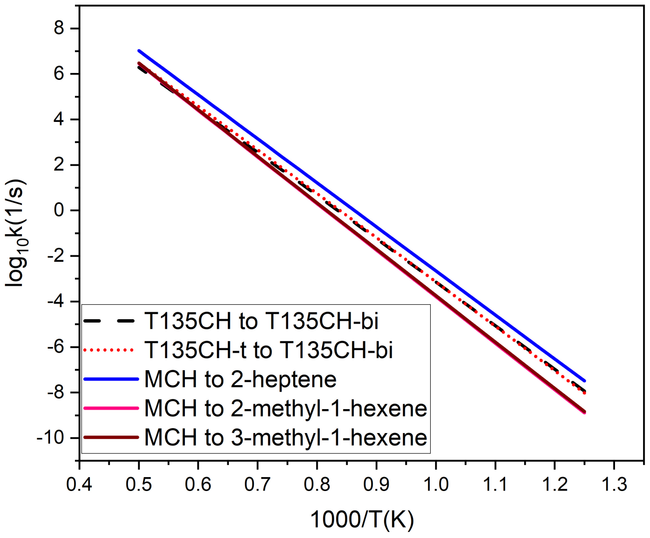

Figure 4.28: Comparison of rate constant of isomerization reaction of T135CH, T135CH-t and MCH. The solid line is for MCH[5].

ring opening process of MCH.

4.3.2.2 H-abstraction reaction by H atom and CH_3 radical

Figure 4.29 and figure 4.30 show rate constants of H-abstraction reactions. Rate constant of H-abstraction by H atom is higher than rate constant of H-abstraction by CH_3 radical.

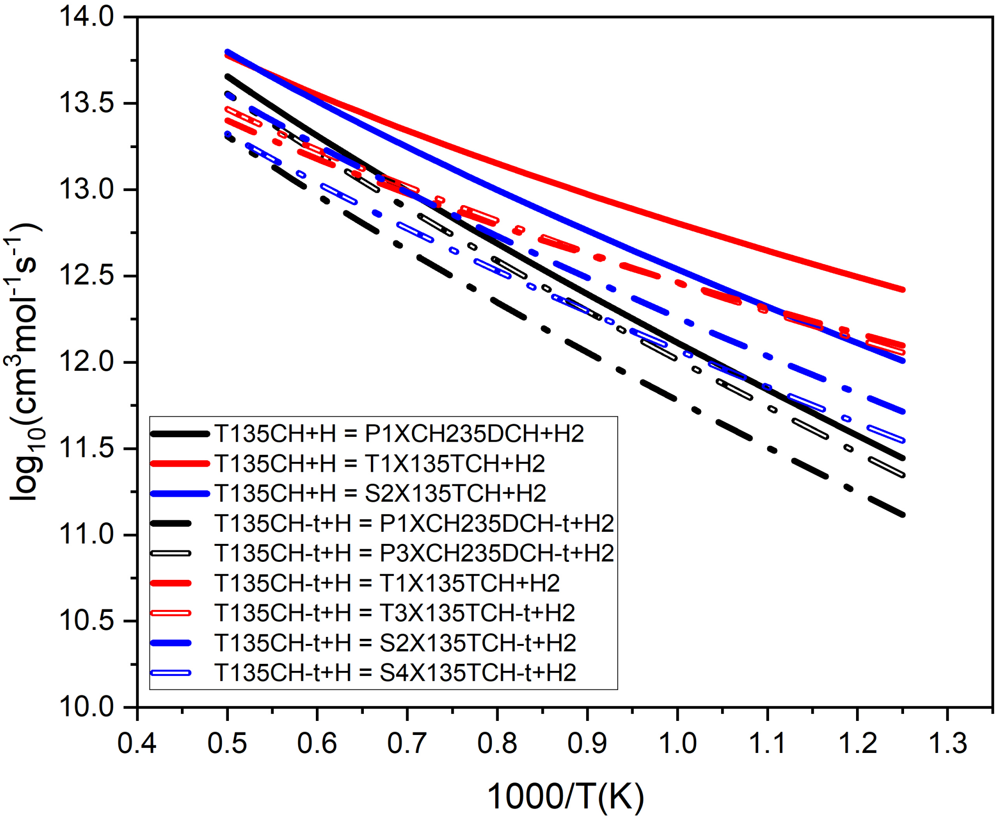

Figure 4.29: Rate constant of H-atom abstraction of T135CH and T135CH-t by H atom. Solid line for T135CH and dash line for T135CH-t. Red line is for tertiary cyclohexane radical, blue line is for secondary cyclohexane radical and black line is for primary cyclohexane radical.

Among the cyclohexane radical, the order of rate constant follows the order:rate of formation of tertiary radical >rate of formation secondary radical >rate of for-

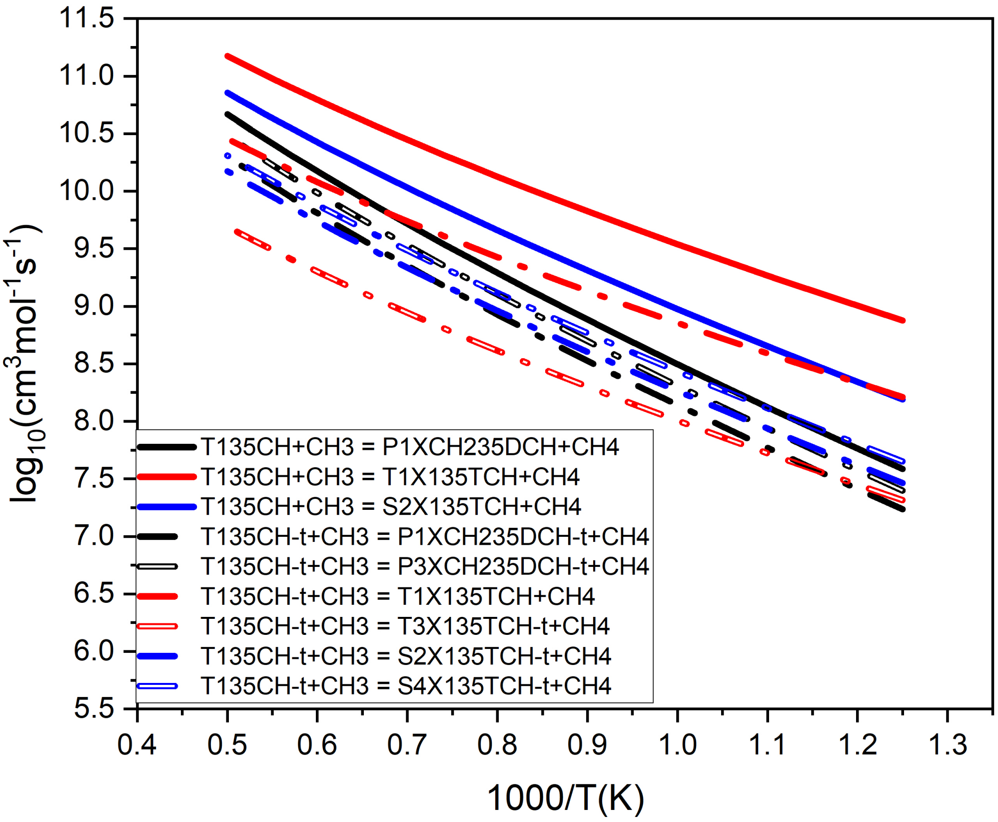

Figure 4.30: Rate constant of H-atom abstraction of T135CH and T135CH-t by CH_3 radical. Solid line for T135CH and dash line for T135CH-t. Red line is for tertiary cyclohexane radical, blue line is for secondary cyclohexane radical and black line is for primary cyclohexane radical.

mation of primary radical.

Rate constant of H-abstraction reaction of T135CH is higher than H-abstraction of T135CH-t.

In figure 4.31, we compare rate of abstraction reaction of T135CH and MCH. Rate constant of H-abstraction reaction associated with T135CH is much higher than H-abstraction reaction associated with MCH.

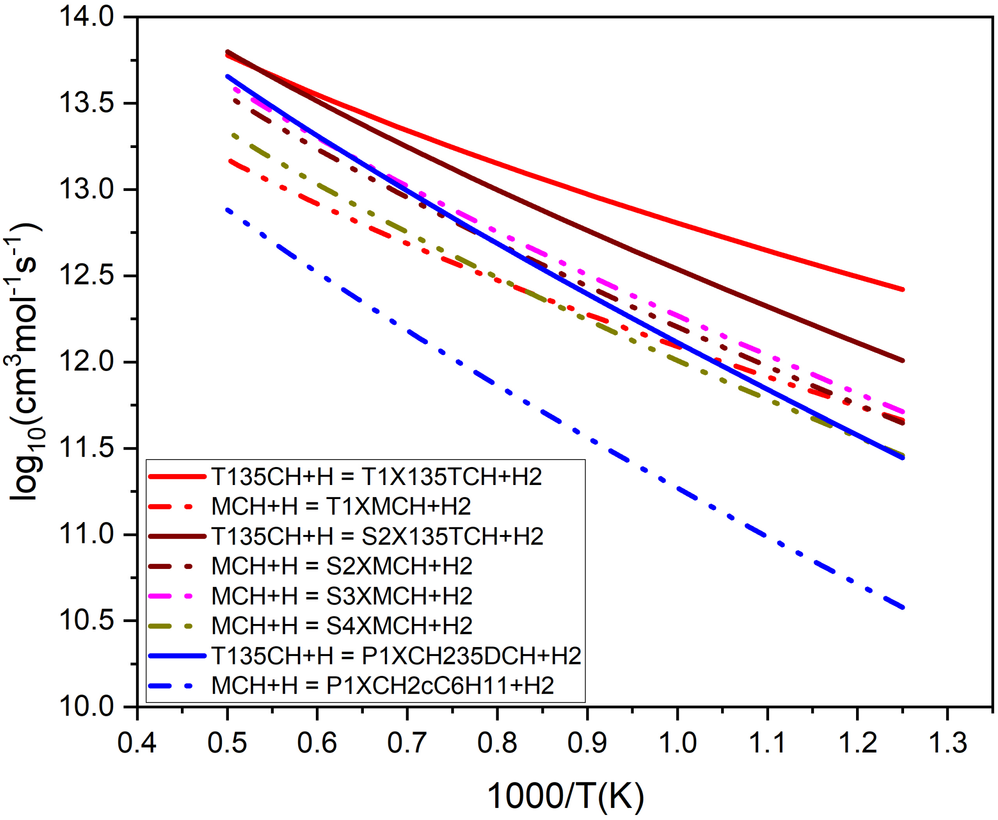

Figure 4.31: Comparison of rate constant of H-abstraction reaction of T135CH and MCH. Dash line is for MCH[6], and solid line is for T135CH. Red line is for tertiary cyclohexane radical, blue line is for primary cyclohexane radical. Other colures represent secondary cyclohexane radicals.

4.3.3 Kinetic parameters

Kinetic parameters A and E_a for all the reactions have been obtained by fitting the calculated rate constants over the temperature range of 800-2000 K. All the kinetic parameters are listed in table 4.8.

Table 4.8: High pressure limit rate parameter of 135TCH decomposition reactions.

No	**Reaction**	**A**	E_a
Unimolecular decomposition and isomerization of IPCH			
1	$T135CH = S1X35DCH + CH_3$	2.26E+16	84525.6
2	$T135CH - t = S1X35DCH + CH_3$	8.70E+16	81691.8
3	$T135CH - t = S1X35DCH - t + CH_3$	5.98E+16	84010.9
4	T135CH=T135CH-bi	6.36E+15	86741.3
5	T135CH-t=T135CH-bi	1.46E+16	88356.9
6	$T135CH - bi = C_7H_{12} - 2E46M - t$	8.30E+10	2189.7
7	$T135CH - bi = C_7H_{12} - 1E46M$	1.45E+10	8763.2
8	$T135CH - bi = C_7H_{12} - 1E24M$	8.41E+10	4491.9
9	$T135CH - bi = C_7H_{12} - 2E46M - t$	8.30E+10	2189.7
10	$T135CH - bi = C_7H_{12} - 1E46M$	1.45E+10	8763.2
11	$T135CH - bi = C_7H_{12} - 1E24M$	8.41E+10	4491.9
abstraction reaction by H atom and CH_3 *radical*			
12	$T135CH + H = S1X35DCH + CH_4$	2.54E+14	36421.4
13	$T135CH + H = P1XCH_235DCH + H_2$	1.24E+15	13584.3
14	$T135CH + H = S2X135TCH + H_2$	9.02E+14	11014.1
15	$T135CH + H = T1X135TCH + H_2$	4.46E+14	8387.8
16	$T135CH + CH_3 = P1XCH235DCH + CH_4$	4.56E+12	18963.5
17	$T135CH + CH_3 = S2X135TCH + CH_4$	3.76E+12	16397.4
18	$T135CH + CH_3 = T1X135TCH + CH_4$	4.47E+12	14157.6
19	$T135CH - t + H = S1X35DCH + CH_4$	1.05E+14	36022
20	$T135CH - t + H = S1X35DCH - t + CH_4$	1.69E+14	36272.4
21	$T135CH - t + H = P1XCH235DCH - t + H_2$	5.44E+14	13481.6
22	$T135CH - t + H = P3XCH235DCH - t + H_2$	9.85E+14	13578.9
23	$T135CH - t + H = S2X135TCH - t + H_2$	5.47E+14	11294.8
24	$T135CH - t + H = S4X135TCH - t + H_2$	2.97E+14	10941.9
25	$T135CH - t + H = T1X135TCH + H_2$	1.71E+14	8051.7
26	$T135CH - t + H = T3X135TCH - t + H_2$	2.35E+14	8694

No	**Reaction**	**A**	E_a
27	$T135CH-t+CH_3=P1XCH235DCH-t+CH_4$	1.91E+12	18854.8
28	$T135CH-t+CH_3=P3XCH235DCH-t+CH_4$	2.96E+12	18956.9
29	$T135CH-t+CH_3=S2X135TCH-t+CH_4$	8.38E+11	16669.2
30	$T135CH-t+CH_3=S4X135TCH-t+CH_4$	1.06E+12	16352.5
31	$T135CH-t+CH_3=T1X135TCH+CH_4$	7.78E+11	13817.8
32	$T135CH-t+CH_3=T3X135TCH-t+CH_4$	1.65E+11	14629.4
decomposition and isomerization of alkylcyclohexane radicals			
33	$P1XCH_{2}35DCH=CH_2-35DCH+H$	5.60E+13	37846.2
34	$P1XCH_{2}35DCH=P7XC_7H_{11}-1E46M$	3.32E+14	32329.8
35	$P1XCH_{2}35DCH=S2X135TCH$	9.75E+12	50041.7
36	$S2X135TCH=D35CH-1E+CH_3$	4.01E+14	31596.5
37	S2X135TCH = T135CH-1E+H	1.24E+14	36954
38	$S2X135TCH=P7XC_7H_{11}-2E46M-t$	1.65E+14	31205
39	T1X135TCH = T135CH-1E+H	2.68E+14	37641.5
40	$T1X135TCH=S6XC_7H_{11}-1E24M$	1.93E+14	30887
41	S1X35DCH = D35CH-1E+H	2.54E+14	38321.2
42	$S1X35DCH=S6XC_7H_{12}-1E4M$	1.54E+14	30310.8
43	$P1XCH_{2}35DCH-t=CH_2-35DCH+H$	9.38E+13	36534.7
44	$P1XCH_{2}35DCH-t=P7XC_7H_{11}-1E46M$	1.55E+14	31556.7
45	$P1XCH_{2}35DCH-t=S2X135TCH-t$	2.90E+13	42754.6
46	$S2X135TCH-t=D35CH-1E+CH_3$	2.07E+14	31695.8
47	$S2X135TCH-t=D35CH-1E-t+CH_3$	1.87E+14	30833.4
48	S2X135TCH-t = T135CH-1E+H	8.43E+13	33816.2
49	$S2X135TCH-t=P7XC_7H_{11}-2E46M-t$	8.24E+13	31441.5
50	$S4X135TCH-t=P7XC_7H_{11}-2E46M-t$	7.60E+13	30575.1
51	S4X135TCH-t = T135CH-3E-t+H	6.81E+13	35823.3
52	$S4X135TCH-t=D35CH-1E-t+CH_3$	2.48E+14	33003.4
53	T3X135TCH-t = T135CH-3E-t+H	2.02E+14	37174.6
54	T3X135TCH-t = S6XC7H11-1E24M	1.01E+14	29649

No	**Reaction**	**A**	E_a
55	$P3XCH_235DCH - t = P7XC_7H_{11} - 1E46M$	1.35E+14	32019.8
56	$P3XCH_235DCH - t = S2X135TCH - t$	9.98E+12	50031.7
57	S1X35DCH-t = D35CH-1E-t+H	2.16E+14	38323.2
58	$S1X35DCH - t = S6XC_7H_{12} - 1E4M$	7.54E+13	29299.3
59	$S1X35DCH - t = S6XC_7H_{12} - 1E4M$	7.54E+13	29299.3
dissociation of alkene and alkyl-cyclohexene			
60	$C_7H_{12} - 2E46M - t = iC_4H_9 + S4XC_5H_9 - 2E$	1.39E+15	66583.1
61	$C_7H_{12} - 2E46M - t + H = T4XC_7H_{11} - 2E46M - t + H_2$	1.27E+14	8878.8
62	$C_7H_{12} - 2E46M - t + CH_3 = T4XC_7H_{11} - 2E46M - t + CH_4$	6.76E+10	12537.4
63	$C_7H_{12} - 2E46M - t = iC_4H_{10} + C_5H_8 - 13E$	9.59E+14	111676.7
64	$C_7H_{12} - 2E46M - t = iC_4H_8 + C_5H_{10} - 2E$	3.34E+15	105683.3
65	$C_7H_{12} - 1E46M = S2XC_5H_{10}2M + aC_3H_5$	6.34E+14	62968.4
66	$C_7H_{12} - 1E46M + H = S3XC_7H_{11} - 1E46M + H_2$	2.09E+14	8248.3
67	$C_7H_{12} - 1E46M + CH3 = S3XC_7H_{11} - 1E46M + CH_4$	3.49E+11	12737.2
68	$C_7H_{12} - 1E46M = C_3H_6 + C_5H_9 - 1E4M$	5.21E+14	104528.7
69	$C_7H_{12} - 1E46M = C_3H_6 + C_5H_9 - 2E4M$	1.99E+15	103580.8
70	$C_7H_{12} - 1E24M = S2XC_5H_{11} + iC_4H_7$	2.88E+15	65989
71	$C_7H_{12} - 1E24M + H = S3XC_7H_{11} - 1E24M + H_2$	1.53E+14	7935.9
72	$C_7H_{12} - 1E24M + CH_3 = S3XC_7H_{11} - 1E24M + CH_4$	2.55E+11	13102.2
73	$C_7H_{12} - 1E24M = C_5H_{10} - 1E + iC_4H_8$	6.37E+14	107422.1
74	$C_7H_{12} - 1E24M = C_5H_{10} - 2E + iC_4H_8$	1.87E+15	106356.9
75	$T135CH - 1E = C_3H_6 + C_5H_7 - 13E2M$	1.15E+15	64679.4
76	$D35CH - 1E = C_3H_6 + C_5H_8 - 13E$	1.32E+15	63850.7
77	$T135CH - 3E - t = C_3H_6 + C_5H_7 - 13E2M$	5.39E+14	63189
78	$D35CH - 1E - t = C_3H_6 + C_5H_8 - 13E$	9.51E+14	62714
decomposition and isomerization of alkenyl radicals			
79	$S6XC_7H_{12} - 1E4M = T4XC_7H_{12} - 1E4M$	5.90E+12	38907.4
80	$S6XC_7H_{12} - 1E4M = S5XC_7H_{12} - 1E4M$	2.28E+13	41524.5
81	$S6XC_7H_{12} - 1E4M = S3XC_7H_{12} - 1E4M$	1.42E+12	17276.3

No	**Reaction**	**A**	E_a
82	$S6XC_7H_{12}-1E4M = P7XC_7H_{12}-1E4M$	1.69E+13	43501.8
83	$T4XC_7H_{12}-1E4M = C_2H_5 + C_5H_7-14E2M$	8.28E+20	37581.9
84	$T4XC_7H_{12}-1E4M = C_2H_3 + C_5H_9-1E2M$	1.76E+21	45037.9
85	$S6XC_7H_{12}-1E4M = C_3H_6 + S4XC_5H_9-1E$	1.59E+14	28176.5
86	$S5XC_7H_{12}-1E4M = CH_3 + C_6H_9-15E3M$	4.19E+16	35785.5
87	$S5XC_7H_{12}-1E4M = aC_3H_5 + C_5H_{10}-2E$	1.22E+16	25231.5
88	$S3XC_7H_{12}-1E4M = nC_3H_7 + C_5H_8-13E$	1.11E+15	38794.1
89	$P7XC_7H_{12}-1E4M = C_2H_4 + P5XC_5H_8-1E4M$	4.16E+14	30821.5
90	$S6XC_7H_{12}-1E4M = P1XCH_2cC_5H_724M$	8.28E+10	4607.1
91	$S6XC_7H_{11}-1E24M = T4XC_7H_{11}-1E24M$	1.85E+13	41820.6
92	$S6XC_7H_{11}-1E24M = S5XC_7H_{11}-1E24M$	3.81E+13	44326.5
93	$S6XC_7H_{11}-1E24M = S3XC_7H_{11}-1E24M$	6.91E+11	17916.4
94	$S6XC_7H_{11}-1E24M = P7XC_7H_{11}-1E24M$	1.06E+07	36282.3
95	$T4XC_7H_{11}-1E24M = CH_3CCH_2 + C_5H_9-1E2M$	7.39E+14	34821.7
96	$T4XC_7H_{11}-1E24M = C_2H_5 + C_5H_6-14E24M$	8.38E+13	29070.7
97	$S6XC_7H_{11}-1E24M = C_3H_6 + S4XC_5H_8-1E2M$	2.81E+14	29498
98	$S5XC_7H_{11}-1E24M = iC_4H_7 + C_5H_{10}-2E$	2.88E+16	25485.8
99	$S5XC_7H_{11}-1E24M = CH_3 + C_6H_8-15E24M$	1.95E+17	37049.4
100	$S3XC_7H_{11}-1E24M = CH_3 + C_7H_{11}-13E2M$	1.19E+14	38601.4
101	$S3XC_7H_{11}-1E24M = nC_3H_7 + C_5H_7-13E2M$	1.10E+14	36141.2
102	$P7XC_7H_{11}-1E24M = C_2H_4 + P5XC_5H_7-1E24M$	4.32E+14	30330.6
103	$S6XC_7H_{11}-1E24M = P1XCH_2cC_5H_6124M$	6.09E+10	6753.3
104	$P7XC_7H_{11}-1E46M = T6XC_7H_{11}-1E46M$	1.65E+13	37190.4
105	$P7XC_7H_{11}-1E46M = T4XC_7H_{11}-1E46M$	3.63E+12	17701.4
106	$P7XC_7H_{11}-1E46M = S5XC_7H_{11}-1E46M$	1.55E+13	37442.8
107	$P7XC_7H_{11}-1E46M = S3XC_7H_{11}-1E46M$	3.56E+11	7612
108	$T6XC_7H_{11}-1E46M = iC_4H_8 + S4XC_5H_9-1E$	2.87E+19	35239
109	$T4XC_7H_{11}-1E46M = C_2H_3 + C_5H_8-1E24M$	1.80E+21	47380.8
110	$T4XC_7H_{11}-1E46M = iC_3H_7 + C_5H_7-14E2M$	7.63E+20	36787

No	**Reaction**	**A**	E_a
111	$S5XC_7H_{11} - 1E46M = CH_3 + C_7H_{11} - 15E4M$	1.07E+14	31656.1
112	$S5XC_7H_{11} - 1E46M = aC_3H_5 + C_5H_9 - 2E4M$	1.55E+13	20150.2
113	$S3XC_7H_{11} - 1E46M = CH_3 + C_7H_{11} - 13E6M$	4.39E+14	38525.8
114	$S3XC_7H_{11} - 1E46M = iC_4H_9 + C_5H_8 - 13E$	2.25E+14	37544.2
115	$P7XC_7H_{11} - 1E46M = C_3H_6 + P5XC_5H_8 - 1E4M$	1.25E+14	27936.1
116	$P7XC_7H_{11} - 2E46M - t = T6XC_7H_{11} - 2E46M - t$	3.79E+13	35948.4
117	$P7XC_7H_{11} - 2E46M - t = T4XC_7H_{11} - 2E46M - t$	1.69E+12	14705.1
118	$P7XC_7H_{11} - 2E46M - t = S5XC_7H_{11} - 2E46M - t$	2.12E+13	39525.4
119	$T6XC_7H_{11} - 2E46M - t = iC_4H_8 + S4XC_5H_9 - 2E$	3.19E+13	20515.9
120	$T4XC_7H_{11} - 2E46M - t = iC_3H_7 + C_5H_7 - 13E2M$	7.07E+15	39290.9
121	$S5XC_7H_{11} - 2E46M - t = CH_3 + C_7H_{11} - 25E4M$	8.51E+13	32009.8
122	$S5XC_7H_{11} - 2E46M - t = CH_3 + C_7H_{11} - 24E6M$	4.74E+13	28619.7
123	$S5XC_7H_{11} - 2E46M - t = CH_3CHCH + C_5H_9 - 2E4M$	1.53E+14	38199.9
124	$P7XC_7H_{11} - 2E46M - t = C_3H_6 + P5XC_5H_8 - 2E4M$	1.99E+14	27842.7
125	$P7XC_7H_{11} - 2E46M - t = S2XC_2H_4cC_5H_735M$	3.01E+11	5421.9
stepwise dehydrogenation of cyclic intermediate			
decomposition of alkyl-cyclopentane radicals			
126	$S2XC_2H_4cC_5H_735M = T3XcC_5H_635M1Et$	2.61E+11	23866.3
127	$T3XcC_5H_635M1Et = S5XC_7H_{11} - 1E24M$	5.75E+13	33575.7
128	$T3XcC_5H_635M1Et = cC_5H_5 - 3E35M1Et + H$	3.33E+14	39032.6
129	$cC_5H_5 - 3E35M1Et + H = S2XcC_5H_4 - 3E35MEt + H_2$	2.51E+14	7230.2
130	$cC_5H_5 - 3E35M1Et + CH_3 = S2XcC_5H_4 - 3E35MEt + CH_4$	1.42E+12	12673
131	$cC_5H_5 - 3E35M1Et + H = T5XcC_5H_4 - 3E35MEt + H_2$	1.66E+14	7118.2
132	$cC_5H_5 - 3E35M1Et + CH_3 = T5XcC_5H_4 - 3E35MEt + CH_4$	1.42E+12	11431.6
133	$cC_5H_5 - 3E35M1Et + H = S5XcC_5H_5 - 3E3M1Et + CH_4$	9.92E+13	32383.4
134	$S2XcC_5H_4 - 3E35MEt = cC_5H_4 - 13E25M + C_2H_5$	4.33E+14	37657.4
135	$T5XcC_5H_4 - 3E35MEt = cC_5H_4 - 13E13M + C_2H_5$	5.61E+14	38410.6
136	$S5XcC_5H_5 - 3E3M1Et = cC_5H_5 - 13E1M + C_2H_5$	4.34E+14	38472.2
137	$cC_5H_4 - 13E25M + H = T2XcC_5H_4 - 13E5M + CH_4$	3.42E+14	43038.8

No	Reaction	A	E_a
138	$cC_5H_5 - 13E5M + H = T2XcC_5H_4 - 13E5M + H_2$	4.12E+14	20162.1
139	$cC_5H_5 - 13E5M + CH_3 = T2XcC_5H_4 - 13E5M + CH_4$	3.58E+12	22370
140	$cC_5H_4 - 13E13M + H = T3XcC_5H_4 - 13E1M + CH_4$	3.71E+14	43026.9
141	$cC_5H_5 - 13E1M + H = T3XcC_5H_4 - 13E1M + H_2$	4.38E+14	20116.4
142	$cC_5H_5 - 13E1M + CH_3 = T3XcC_5H_4 - 13E1M + CH_4$	3.82E+12	22393.8
143	$P1XCH_2cC_5H_724M = T4XcC_5H_6124M$	1.05E+12	23001.8
144	$T4XcC_5H_6124M = S5XC_6H_9 - 1E24M$	7.44E+13	34160
145	$T4XcC_5H_6124M = cC_5H_5 - 3E135M + H$	2.32E+14	39229.3
146	$cC_5H_5 - 3E135M + H = S2XcC_5H_4 - 3E135M + H_2$	2.58E+14	7393
147	$cC_5H_5 - 3E135M + CH_3 = S2XcC_5H_4 - 3E135M + CH_4$	1.42E+12	12961.3
148	$cC_5H_5 - 3E135M + H = T5XcC_5H_4 - 3E135M + H_2$	1.73E+14	7204
149	$cC_5H_5 - 3E135M + CH_3 = T5XcC_5H_4 - 3E135M + CH_4$	1.40E+12	10944.3
150	$cC_5H_5 - 3E135M + H = S5XcC_5H_5 - 3E13M + CH_4$	9.69E+13	30506.6
151	$S2XcC_5H_4 - 3E135M = cC_5H_4 - 13E35M + CH_3$	5.54E+14	39903
152	$T5XcC_5H_4 - 3E135M = cC_5H_4 - 13E13M + CH_3$	5.21E+14	39996.4
153	$S5XcC_5H_5 - 3E13M = cC_5H_5 - 13E1M + CH_3$	4.55E+14	40129.5
154	$cC_5H_4 - 13E35M + H = T2XcC_5H_4 - 13E5M + CH_4$	3.42E+14	41038.8
155	$P1XCH_2cC_5H_6124M = T4XcC_5H_51124M$	2.23E+12	21827.4
156	$T4XcC_5H_51124M = cC_5H_4 - 1E1344M + H$	4.01E+14	38905.4
157	$T4XcC_5H_51124M = cC_5H_4 - 3E1355M + H$	7.42E+14	37941.6
158	$cC_5H_4 - 1E1344M + H = S3XcC_5H_4 - 1E144M + CH_4$	9.13E+13	32389.4
159	$S3XcC_5H_4 - 1E144M = cC_5H_4 - 13E14M + CH_3$	6.02E+14	39712.2
160	$cC_5H_4 - 3E1355M + H = S2XcC_5H_3 - 3E1355M + H_2$	2.47E+14	7432.1
161	$cC_5H_4 - 3E1355M + CH_3 = S2XcC_5H_3 - 3E1355M + CH_4$	1.52E+12	13062.5
162	$S2XcC_5H_3 - 3E1355M = cC_5H_2 - 13E1355M + H$	1.32E+14	45383.7
163	$cC_5H_4 - 13E14M + H = T4XcC_5H_4 - 13E1M + CH_4$	1.18E+14	42859.9
164	$cC_5H_5 - 13E1M + H = T4XcC_5H_4 - 13E1M + H_2$	5.27E+14	20416.5
165	$cC_5H_5 - 13E1M + CH_3 = T4XcC_5H_4 - 13E1M + CH_4$	4.74E+12	22544.8
166	$cC_5H_5 - 13E5M = cC_5H_5 - 13E1M$	1.50E+13	24466.4

No	**Reaction**	**A**	E_a
decomposition of alkylcyclohexene			
167	$T135CH-1E=C_3H_6+C_5H_7-13E2M$	1.15E+15	64679.4
168	$T135CH-1E+H=S6X135TCH-1E+H_2$	2.68E+14	8395.3
169	$T135CH-1E+CH_3=S6X135TCH-1E+CH_4$	1.84E+12	13694
170	$T135CH-1E+H=T3X135TCH-1E+H_2$	2.06E+14	5440.6
171	$T135CH-1E+CH_3=T3X135TCH-1E+CH_4$	2.74E+12	10922.8
172	$S6X135TCH-1E=D13CH-15E+CH_3$	1.44E+15	44229.1
173	$D13CH-15E+H=T3X13DCH-15E+H_2$	5.53E+14	4488.1
174	$D13CH-15E+CH_3=T3X13DCH-15E+CH_4$	2.05E+12	10701.1
175	$D13CH-15E+H=S4X13DCH-15E+H_2$	3.18E+14	6787.3
176	$D13CH-15E+CH_3=S4X13DCH-15E+CH_4$	2.69E+12	12317.3
177	T3X13DCH-15E = m-xylene+H	7.16E+13	31054
178	$S4X13DCH-15E=A1CH_3+CH_3$	1.18E+14	24081
179	S4X13DCH-15E = m-xylene+H	4.13E+13	29037
180	T3X135TCH-1E = T135CH-13E+H	9.63E+13	50520.6
181	$T135CH-13E+H=S6X135TCH-13E+H_2$	3.62E+14	6714
182	$T135CH-13E+CH_3=S6X135TCH-13E+CH_4$	4.48E+12	10400.6
183	$S6X135TCH-13E=m-xylene+CH_3$	1.38E+14	24259.7
184	$D35CH-1E=C_3H_6+C5H8-13E$	1.32E+15	63850.7
185	$D35CH-1E+H=S6X35DCH-1E+H_2$	2.77E+14	8768.1
186	$D35CH-1E+CH_3=S6X35DCH-1E+CH_4$	6.05E+12	14023.3
187	$D35CH-1E+H=T3X35DCH-1E+H_2$	1.73E+14	5810.8
188	$D35CH-1E+CH_3=T3X35DCH-1E+CH_4$	3.00E+12	11080.8
189	$S6X35DCH-1E=MCH-35E+CH_3$	1.56E+15	44298.7
190	$MCH-35E+H=T1XMCH-35E+H_2$	3.43E+14	5026.4
191	$MCH-35E+CH_3=T1XMCH-35E+CH_4$	1.99E+12	10714
192	$T1XMCH-35E=A1CH_3+H$	2.77E+13	30426
193	$MCH-35E+H=S2XMCH-35E+H_2$	3.07E+14	6775.4
194	$MCH-35E+CH_3=S2XMCH-35E+CH_4$	3.50E+12	12193.3

No	**Reaction**	**A**	E_a
195	$S2XMCH-35E=A1+CH_3$	2.93E+14	24625.4
196	$S2XMCH-35E=A1CH_3+H$	5.67E+13	29746.4
197	T3X35DCH-1E = D13CH-15E+H	1.25E+14	51019.4
Isomerization of T135CH to different trimethylcyclohexane			
198	$D13CH+H=S1X35DCH+H_2$	3.41E+14	11222.3
199	$D13CH+CH_3=S1X35DCH+CH_4$	1.52E+12	16667.2
200	S1X35DCH = S2X35DCH	3.09E+13	43108.3
201	$T124CH+H=S2X35DCH+CH_4$	8.74E+13	36224.7
202	$D13CH+H=T3X13DCH+H_2$	3.22E+14	8568.4
203	$D13CH+CH_3=T3X13DCH+CH_4$	2.30E+12	14155.4
204	$T133CH+H=T3X13DCH+CH_4$	8.49E+13	34521.6
205	$D13CH+H=S3XMCH+CH_4$	1.79E+14	36485
206	$MEtCH=T1XMCH+C_2H_5$	4.32E+15	73776.8
207	$D13CH-t+H=S1X35DCH-t+H_2$	3.36E+14	11044.5
208	$D13CH-t+CH_3=S1X35DCH-t+CH_4$	2.80E+12	16434.3

Note $k(T)=A\exp(-E_a/RT)$, unit is cm^3, mol, s, cal.

4.3.4 Experiment and Simulation

The pyrolysis experiments have been carried out for temperature ranging from 1017- 1542 K and pressure ranging from 13.35– 23.46 bar. The observed dwell times in the present study have been found to be in the range of 1.40-1.54 msec. Typical gas chromatograms of post shock mixture of 135TCH obtained using GC-FID/FID, are shown in figure 4.32 and figure 4.33.

The major products observed in the post-shocked mixture have been the following: methane, ethene, acetylene, ethane, propene, allene, propyne, 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, cyclopentadiene, benzene.

The minor products observed are the following: vinylacetylene, toluene, butene, 1,3-butadiyne, butyne, methylbutadiene, 3-methylpentadiene, 2-methylpentadiene, 5-methylcyclopentadiene, 1-methylcyclopentadiene, cyclohexadiene, 1,3-dimethylcyclohexane-cis, 1,3-dimethylcyclohexane-trans, styrene, 3,3,5-trimethylcyclohexane, 1,2,4-trimethylcyclohexane, and 1-ethyl,1-methylcyclohexane.

As discussed in the previous chapter (3.3.4), we used the carbon balance method to estimate initial reaction concentration of the reactant.

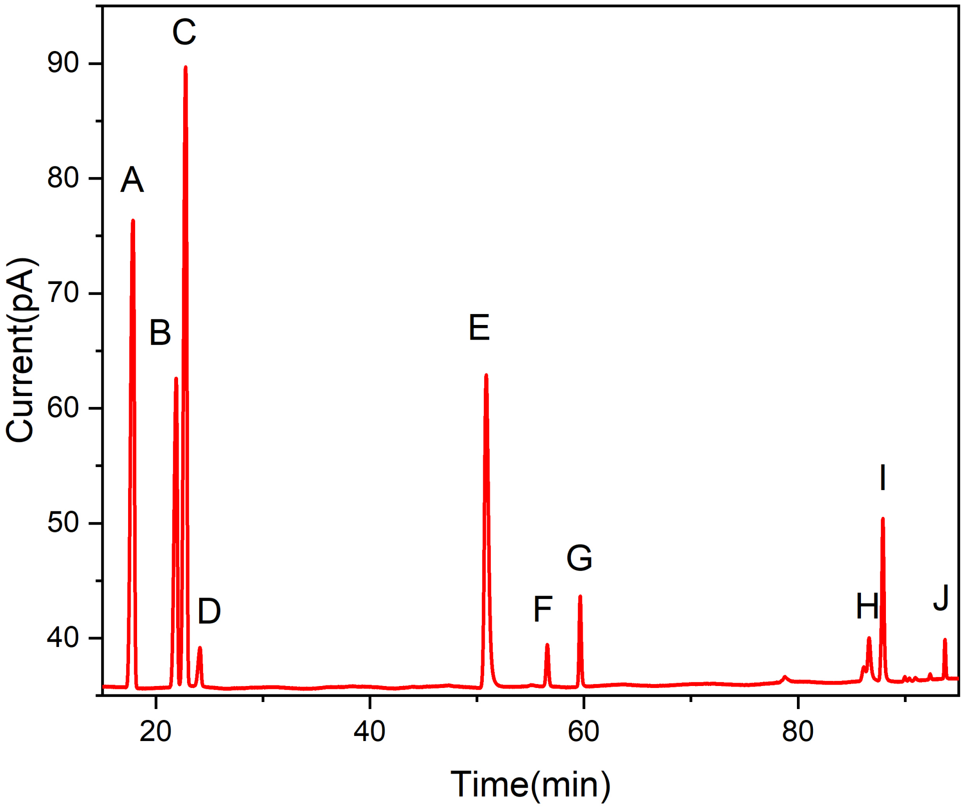

Figure 4.32: Chromatogram from GC front-FID (lower boiler species). Peaks are assigned (A) methane, (B) ethene, (C) acetylene, (D) ethane, (E) propene, (F) propane, (F) allene, (G) propyne, (H) vinylacetylene, (I) 1,3-butadiene, (J) 1-butyne. Only major products are assigned here.

The following equation has been used to calculate initial concentration:

$$[135TCH]_0 = [135TCH]_t + \sum_{i=1}^{30} \frac{n_i[P_i]_t}{9} \tag{4.1}$$

Here, $[135TCH]_0$ is the initial concentration of IPCH, $[135TCH]_t$ is the concentration of 135TCH after time t, n_i is the no. of carbon in the ith product, $[P_i]_t$ is the concentration of the ith product after time t. The distribution of the nor-

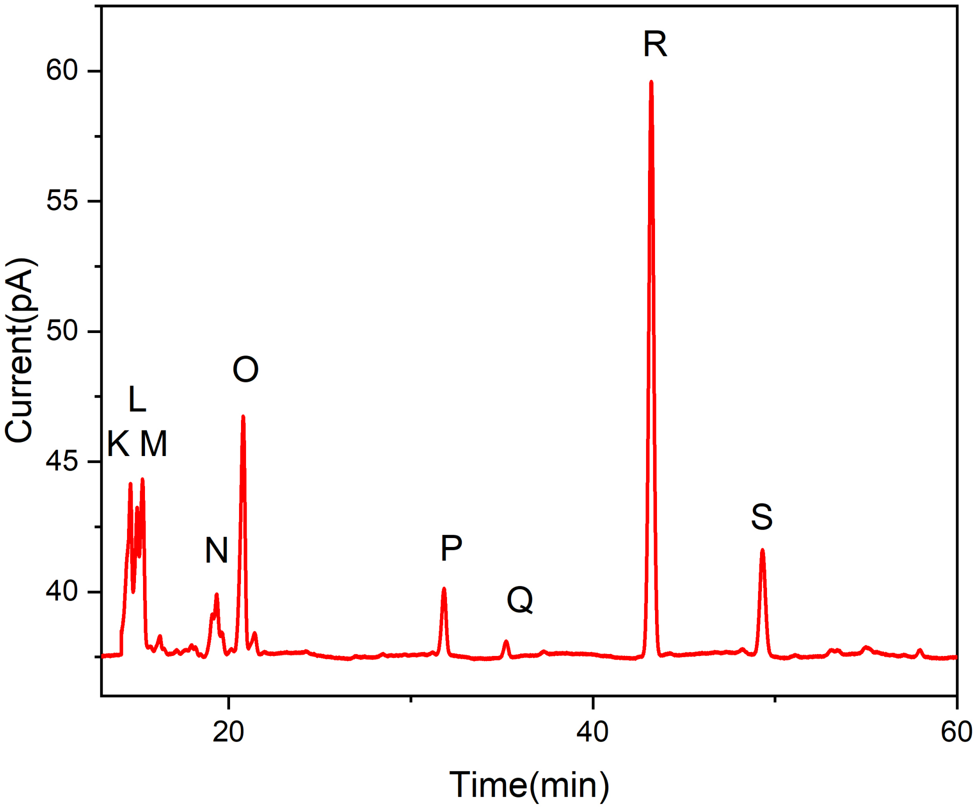

Figure 4.33: Chromatogram from GC back-FID (higher boiler species). Peaks are assigned (K) 1,3-pentadiene, (L) 1,4-pentadiene, (M) cyclopentadiene, (N) methylcyclopentadiene, (O) benzene, (P) toluene, (Q) 1,3-dimethylcyclohexane-cis, (R) 1,3,5-trimethylcyclohexane-cis, and (R) 1,3,5-trimethylcyclohexane-trans. Only major products are assigned here.

malized concentration of the reactants and all the products in the experimental temperature range are given in the next sections.

4.3.4.1 Major species

Figure 4.34 shows the normalized mole fractions profiles for the major species.

The products concentration profile shows that methane is the most abundant product formed by the decomposition of 1,3,5-trimethylcyclohexane (135TCH). The present kinetic model reasonably predicts the decomposition of 135TCH and

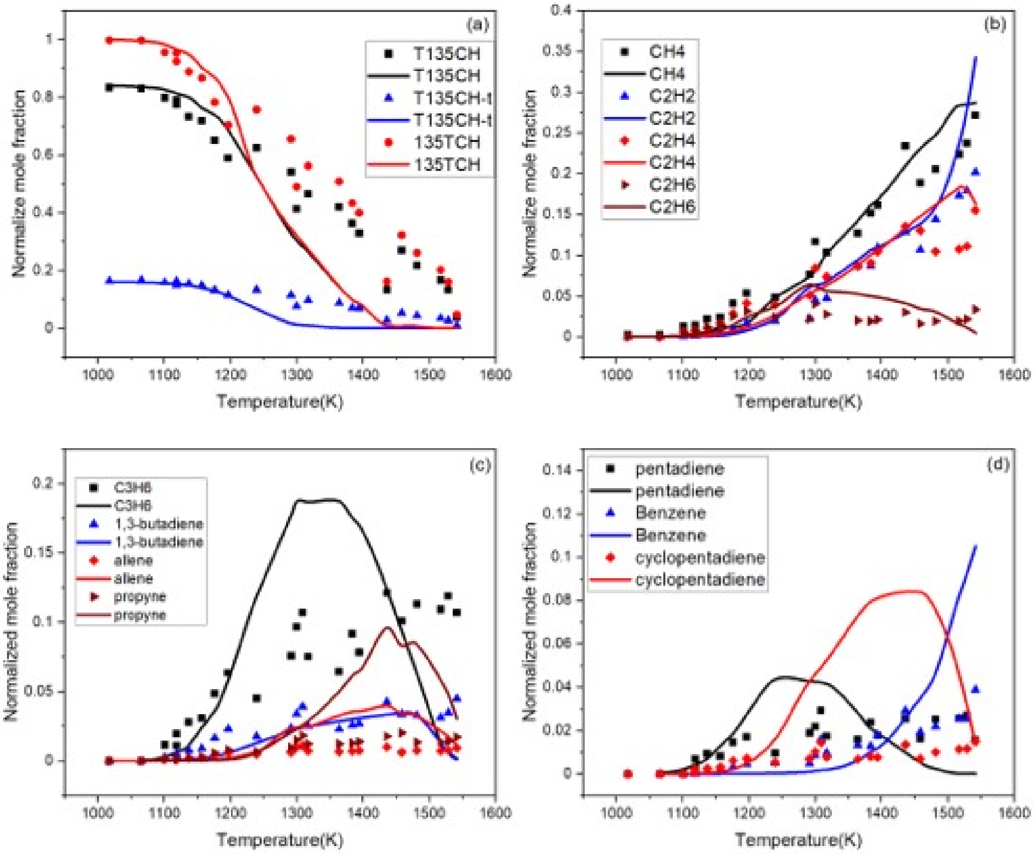

Figure 4.34: Experimental (symbols) and modelling (lines) results of major species of 135TCH pyrolysis at the temperature range. (a) T135CH(cis-1,3,5-trimethylcyclohexane, T135CH-t (trans-1,3,5-trimethycyclohexane), 135TCH (total 1,3,5-trimethylcyclohexane). (b) CH_4 (methane), C_2H_4 (ethene), C_2H_2 (acetylene), C_2H_6 (ethane). (c) C_3H_6 (propane), 1,3-butadiene, allene, propyne. (d) Pentadiene, cyclopentadiene and benzene.Normalized mole fraction for reactant $= \frac{[135TCH]_t}{k[135TCH]_0}$. Normalization mole fraction for products $= \frac{[P_i]_t}{k[135TCH]_0}$. $k = \frac{[135TCH]_t}{[135TCH]_0} + \sum_i^{30} \frac{[P_i]_t}{[135TCH]_0}$.

formation of all the major products.

135TCH (fig 4.34(a)) starts to decompose around 1100 K and completely decompose at the temperature higher than 1500 K. Our model little overestimates the decomposition of 135TCH at the temperature above 1200 K.

Methane (fig 4.34(b)) starts forming at temperature around 1100 K and its concentration keeps increasing with temperature. Our kinetic model predicts the formation of methane quite well. Ethene (fig 4.34(b)) also starts forming around 1100 K temperature and its amount keeps increasing with temperature. Present model predicts ethene well over the temperature range. Acetylene (fig 4.34(b)) starts forming around 1200 K temperature and its concentration keeps increasing with temperature. Present model over-predicts formation of acetylene at temperature above 1500 K. Ethane (fig 4.34(b)) also starts forming at the same temperature as methane but amount of ethane formed is very less compared to methane.

Propene (fig 4.34(c)) starts forming at the temperature around 1100 K, hit the peak at the temperature around 1300 K and then remains constant with the temperature. Present models predict formation of propene well till 1200 K, after that it little over-predicts till 1450 K and under-predicts beyond that. Present model predicts the formation of 1,3-butadiene (fig 4.34(c)) quite well whereas it over-predicts the formation of allene and propyne very little beyond 1300 K.

Benzene (fig 4.34(d)) is the most abundant aromatic product and it starts forming at the temperature around 1250 K and concentration of benzene keep on increases with temperature within our experimental conditions. Our kinetic model predicts this trend quite well and overestimates benzene formation beyond 1500 K temperature. Cyclopentadiene, see fig 4.34(d)), is other important cyclic product which also starts forming at the same temperature (1150 K) and our model overestimates its formation beyond 1250 K. We have also detected both 1,3-pentadiene and 1,4-pentadiene in our experiment and in the figure (fig 4.34(d)) we presented total concentration of pentadiene. Present kinetic model slightly over-predicts the formation of pentadiene at low temperature.

4.3.4.2 Minor species

Figure 4.35 shows the normalized mole fraction profiles for the minor species.

Vinylacetylene, 1,3-butydiyne, butyne and methylbutadiene (fig 4.35(a)) are predicted well by our model whereas butene (fig 4.35(a)) is little overestimated by the model.

For the methylpentadiene (fig 4.35(b)) the disagreement with simulation and experiment is high at 1300 K temperature. Toluene and styrene are the other two aromatic products we have detected in our experiment. Our kinetic model slightly underestimates toluene formation whereas as it predicts styrene formation quite well (fig 4.35(b)). Methylcyclopentadiene (fig 4.35(b)) formation is also predicted quite well by our model at low temperature. Formation of cyclohexadiene (fig 4.35(b)) underpredicted by our model.

We have also detected few isomers of trimethylcyclohexane in our experiments (fig 4.35(c)) namely 1,1,3-trimethylcyclohexane; 1,2,4-trimethylcyclohexane and 1-ethyl,1-methylcyclohexane. Our model fails to predict those. This is because of the lack of reaction mechanism of the isomerization processes (isomer-

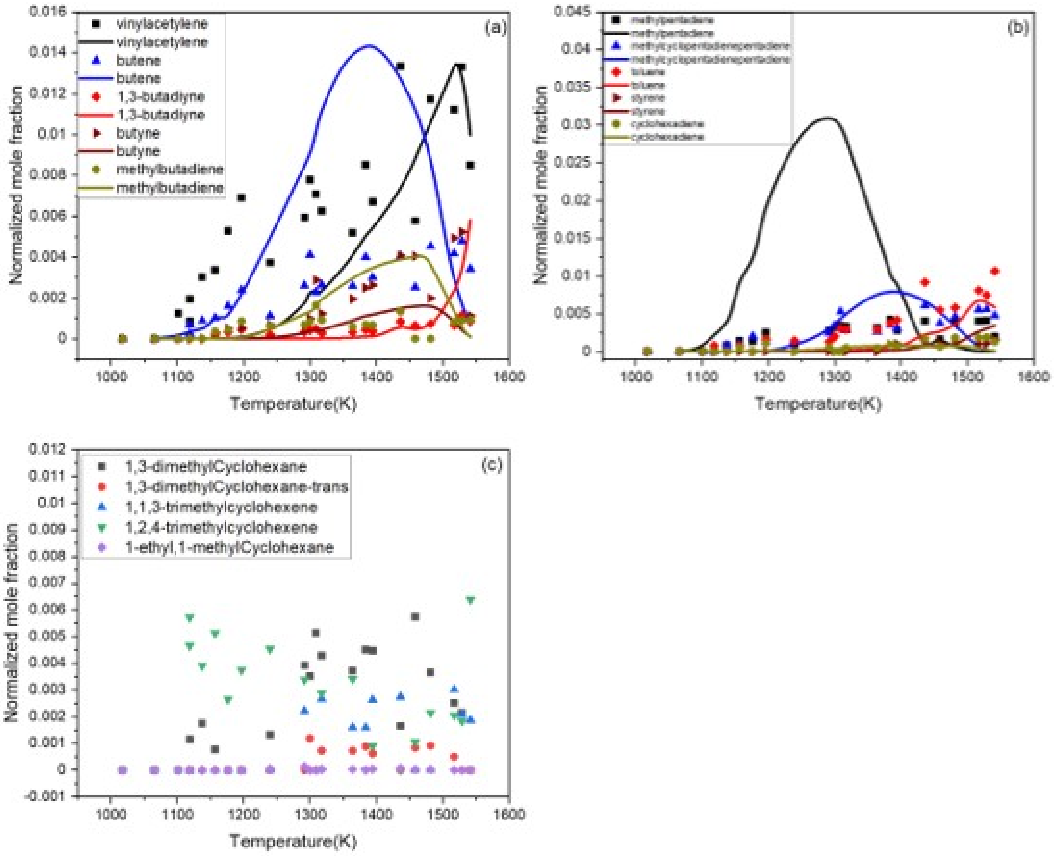

Figure 4.35: Experimental (symbols) and modelling (lines) results of minor species of 135TCH pyrolysis at the temperature range. (a) Vinylacetylene, butene, butadiyne, butyne, methylbutadiene. (b) methylpentadiene, methylcyclopentadiene, cyclohexadiene, toluene, styrene. (c) 1,3-dimethylcyclohexane(cis), 1,3-dimethylcyclohexane(trans), 1,1,3-trimethylcyclohexane, 1,2,4-trimethylcyclohexane, 1-ethyl, 1-methylcyclohexane. Normalization mole fraction $= \frac{[P_i]_t}{k[135TCH]_0}$. $k = \frac{[135TCH]_t}{[135TCH]_0} + \sum_i^{30} \frac{[P_i]_t}{[135TCH]_0}$.

ization between 1,3,5-trimethylcyclohexane, 1,2,4-trimethylcyclohexane and 1,1,3-trimethylcyclohexane) in the present model as well as in the literature. Our model fails to predict the formation of dimethylcyclohexane (both cis and trans) (fig 4.35(c)) as well.

4.3.4.3 ROP and sensitivity analysis

To understand the important pathways of 135TCH consumption as well as the various dissociation paths of unstable radicals and formations of aromatic products reaction flux analysis and sensitivity analysis have been performed.

Consumption of 135TCH

To identify the main pathway of 135TCH consumption, flux analysis has been performed.

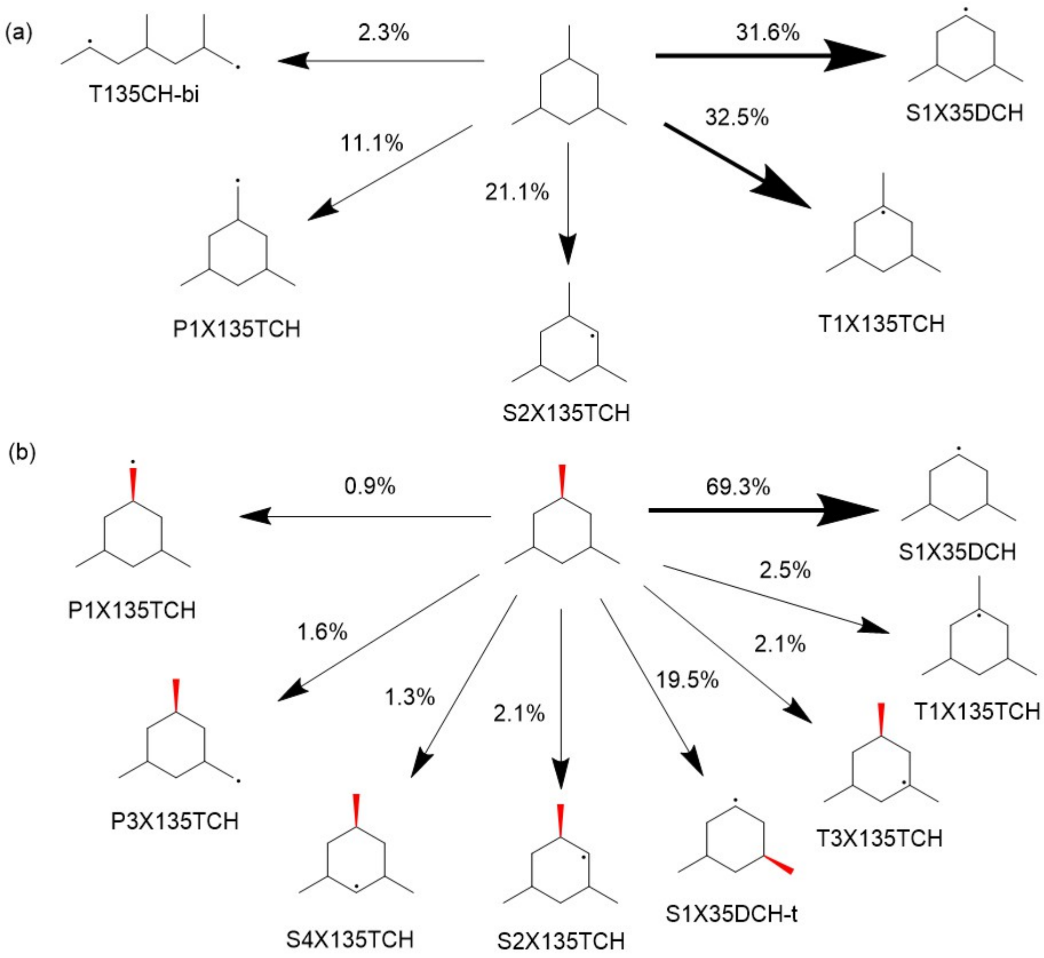

Figure 4.36: Reaction pathways consuming 135TCH at 1394 K temperature with approximately 60% 135TCH conversion. (a) pathways of the consumption of T135CH and (b) pathways of the consumption of T135CH-t. The number above the arrow indicates the respective percentage contribution to the overall consumption.

Figure 4.36 shows the reaction flux of 135TCH at 1394 K revealing the main pathways of 135TCH consumption. T135CH (fig 4.36(a)) is mostly consumed by unimolecular dissociation reactions and H-abstraction reactions by H atom and CH_3 radical. The contribution of H-abstraction reaction has the most important role, the dominant route being the formations of tertiary radical, T1X135TCH (i.e., 32.5%) secondary radical (S2X135TCH, 21.1%) and primary radical (P1X135TCH, 11.1%). Unimolecular dissociation reaction also plays a major role in 135TCH consumption (31.6 %). The ring opening isomerization process has very minor role in 135TCH consumption and had only 2.3 % overall contribution. T135CH-t (ig 4.36(b)) consumption is dominated by unimolecular dissociation reaction. Axial CH_3 group elimination reaction is the dominant route (69.3%) followed by equatorial CH_3 group elimination (19.5%). Consumption by H-abstraction reaction plays very minor role in the overall thermal decomposition of T135CH-t. To further clarify the effect of unimolecular decomposition and H- atom abstraction reactions on 135TCH consumption, the sensitivity analysis of 135TCH has been done at 1394K.

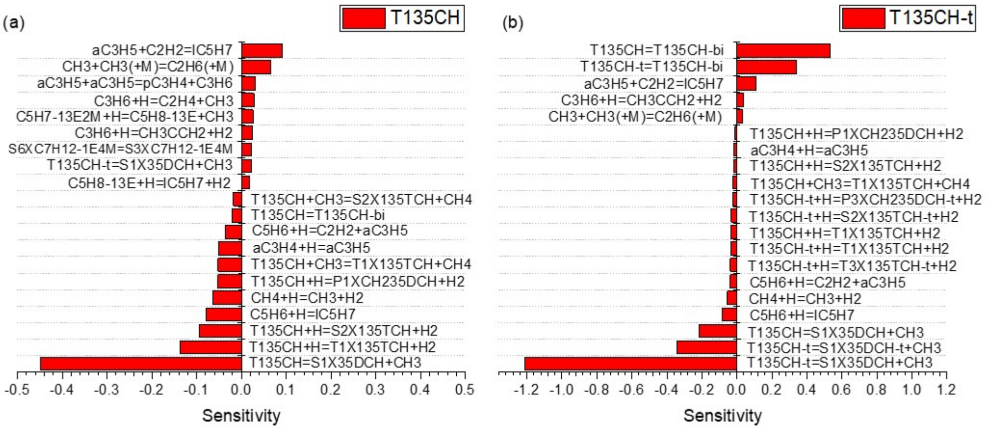

Figure 4.37: Normalized sensitivity analysis of 135TCH at 1394K temperature with approximately 60% 135TCH conversion. (a) sensitivity of T135CH and (b) sensitivity of T135CH-t. Only the top 20 sensitive reactions have been shown.

Figure 4.37 shows the sensitivity analysis. The most sensitive reaction of T135CH (fig 4.37(a)) decomposition is the CH_3 elimination channel followed by the abstraction reaction to form T1X135TCH. The positive effects of these reactions on T135CH consumption occurs because these are the direct consumption channel of 135TCH. H-atom abstraction reactions of 135TCH are rapid when more H atom/CH_3 radical are added into the system. This explanation is according to the negative effect of H/CH_3 abstraction by CH_3, C_3H_6, $C_5H_8 - 13E$ etc on T135CH consumption. Allylic radical (aC_3H_5) also plays a role in T135CH consumption. Consumption reactions of aC_3H_5 ($aC_3H_5 + C_2H_2 = lC_5H_7$, $aC_3H_5 + aC_3H_5 = pC_3H_4 + C_3H_6$) has most negative effect on T135CH consumption whereas formation reactions of aC_3H_5 ($C_5H_6 + H = aC_3H_5 + C_2H_2$, $aC_3H_4 + H = aC_3H_5$) has positive effect on 135TCH consumption.

Decomposition of alkylcyclohexyl radicals

From initial consumption process of 135TCH, different alkylcyclohexane radicals are formed. To understand the detailed process of the pyrolysis of 135TCH, reaction flux analysis of those radicals (major intermediate after initials decomposition of 135TCH) has been performed at 1394 K. Figure 4.38 shows the pyrolysis consumption of S1X35DCH, S2X135TCH, T1X135TCH, and P1X135TCH at 1394 K.

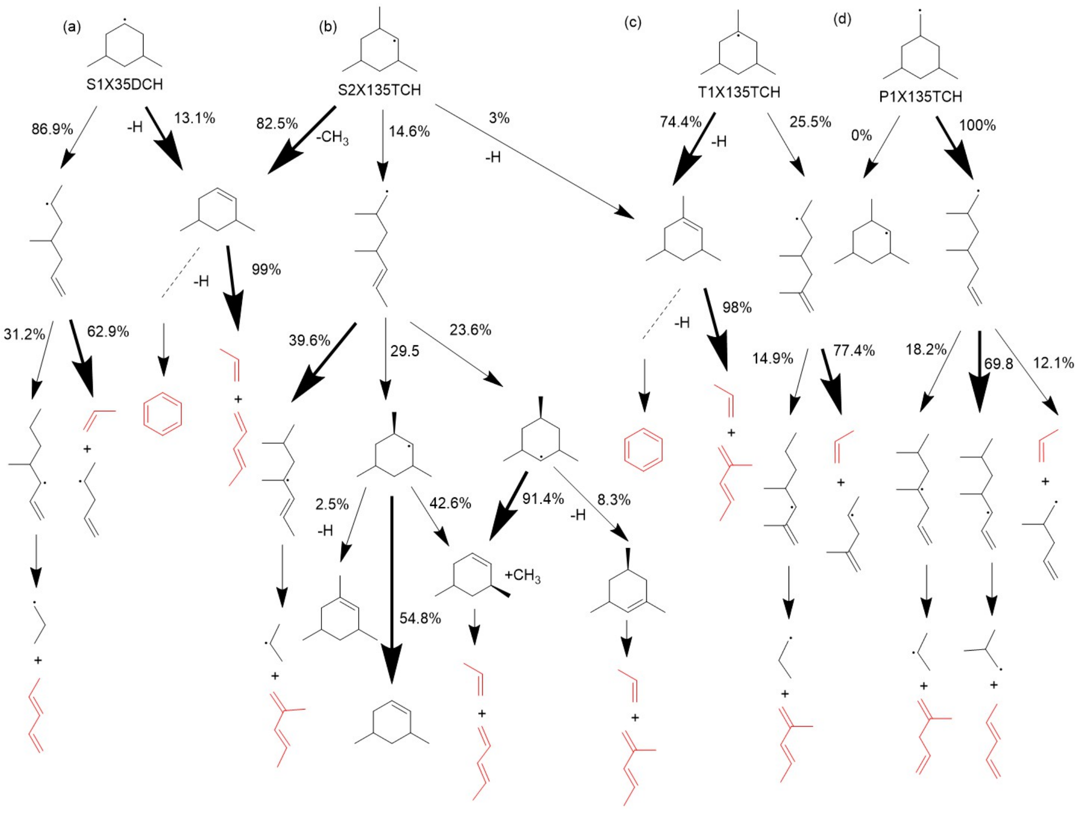

Figure 4.38: Reaction flux analysis of (a) S1X35DCH, (b) S2X135TCH, (c) T1X135TCH and (d) P1X135TCH at 1394 K. Species labelled with red were detected in experiment. The number above the arrow indicates the respective percentage contribution to the overall contribution.

S1X35DCH (fig 4.38(a)) mainly isomerizes (86.9%) to $S6XC_7H_{12}-1E4M$ by ring opening. H elimination to form dimethylcyclohexene has less contribution (13.1%).

For S2X135TCH (fig 4.38(b)), CH_3 elimination process predominates (82.5%) and leads to dimethylcyclohexene. H elimination to form trimethylcyclohexene has less contribution (3%). S2X135TCH also isomerizes to alkenyl radical by ring-opening (14.6%).

For T1X135TCH (fig 4.38(c) H elimination to form trimethylcyclohexene (74.4%) is the dominant channel followed by ring-opening to form alkenyl radical (25.5%).

PIX135TCH (fig 4.38(d)) predominately isomerizes to alkenyl radical by ring-opening. Alkenyl radical which is formed from those processes either undergoes direct $\beta-C-C$ dissociation or isomerization (intermolecular 1,4-H shift) followed by $\beta-C-C$ dissociation. Although $P7XC_7H_{11}-2E46M-t$ (fig 4.38(b) which is formed by the ring-opening isomerization of S2X135TCH) can form secondary trans cyclohexane radical by ring closing. Dimethylcyclohexene, trimethylcyclohexene which are formed from above mentioned processes can either lead to benzene/toluene by step-wise dehydrogenation process or dissociate to alkene/ diene (reverse DA reaction).

In summary, the ring-opening isomerization of alkylcyclohexane radicals form various alkenyl radicals. They lead to diene of methylpentadiene (2-methyl-1,3-pemtadiene, 2-methyl-1,4-pemtadiene), pentadiene(1,3-pentadiene); alkene (propene); radicals of CH_3, C_3H_7 etc. Dehydrogenation/dealkylation of alkylcyclohexane radicals forms dimethycyclohexene and trimethylcyclohexene. They lead to diene of methylpentadiene, pentadiene; alkene of propene; and aromatic intermediate (benzene, toluene).

Reaction pathway analysis for benzene, toluene, and styrene

Figure 4.39 shows the reaction pathways analysis of benzene with 135TCH conversion of approximately 85% at 1482 K. Benzene is produced from multiple channels in 135TCH pyrolysis.

Benzene is mainly formed by the addition of resonance stabilized radicals. The most dominant channel is the addition of propargyl radical with propyne ($pC_3H_4+C_3H_3$, 45.5%). Other important reaction for benzene is from resonance stabilized radicals: $aC_3H_4+C_3H_3$ (17.6 %) $C_3H_3+C_3H_3$ (11.4%), $C_4H_4+C_2H_3$ (0.4%) and $C_4H_4+C_2H_2$ (0.2%). Fulvene also plays a significant role in the benzene formation and is the 2nd most dominant channel of benzene formation (22.8%). Benzene formation by dehydrogenation from cyclohexadienyl ($S1XcC_6H_7-24E$) radical has only 0.1% contribution. From these results it can be concluded that for 135TCH, dehydrogenation/dealkylation of cyclic intermediate do not contribute to benzene formation.

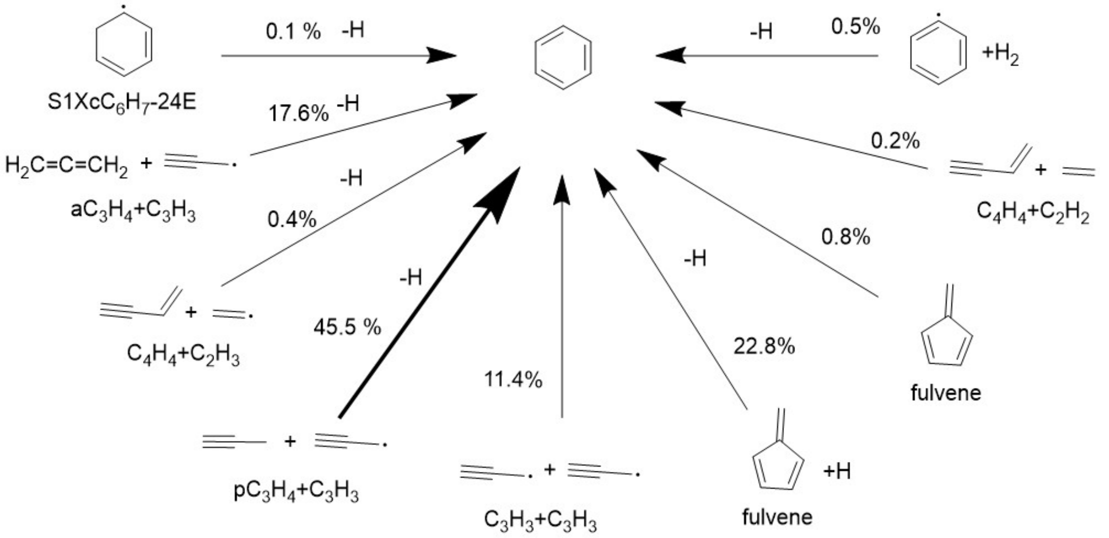

Figure 4.39: Reaction pathways analysis of benzene in 135TCH pyrolysis at 1482 K with 135TCH conversion of approximately 85%.

The sensitivity analysis for benzene is shown in figure 4.40.

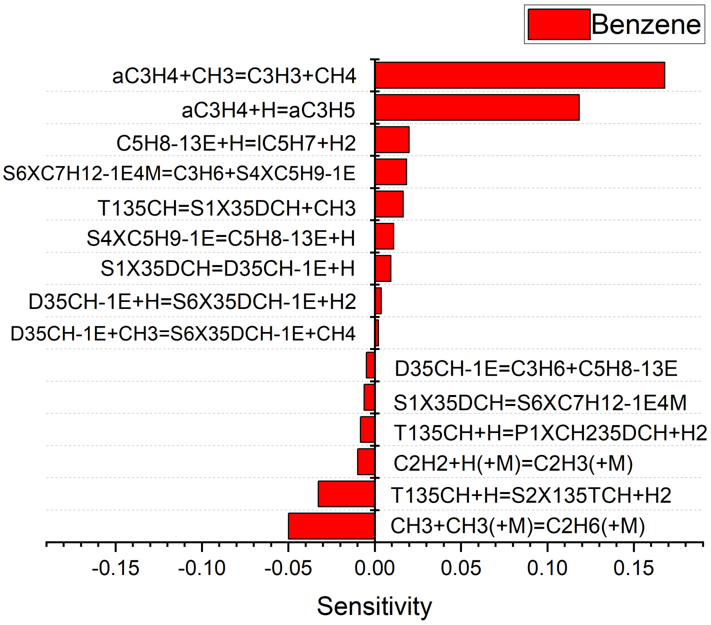

Figure 4.40: Normalized sensitivity analysis of benzene at 1482 K temperature with approximately 85% 135TCH conversion.

Allene (aC_3H_4) play a key role in the formation of benzene. Its addition reaction with CH_3 ($aC_3H_4+CH_3$) is the most sensitive reaction has the positive effect on benzene formation followed by its addition reaction with H (aC_3H_4+H). Two CH_3 addition reaction (CH_3+CH_3) is the most sensitive reaction which has negative effect on benzene formation. H-abstraction reaction of T135CH has negative effect on benzene formation. Ring-opening of cyclohexane radical (S1X35DCH) has the negative effect on benzene formation whereas H elimination reaction of it has positive effect on benzene formation. Formation of S1X35DCH (resulting from the unimolecular dissociation of T135CH) also has the positive effect on benzene formation. Dissociation of cyclohexene (D35CH-1E) has the negative effect on benzene formation whereas H-abstraction reaction of it has positive effect on benzene formation. Unimolecular dissociation of T135CH also has positive effect on benzene formation.

Figure 4.41 shows the reaction pathway of toluene and styrene with 135TCH conversion of approximately 85% at 1482 K.

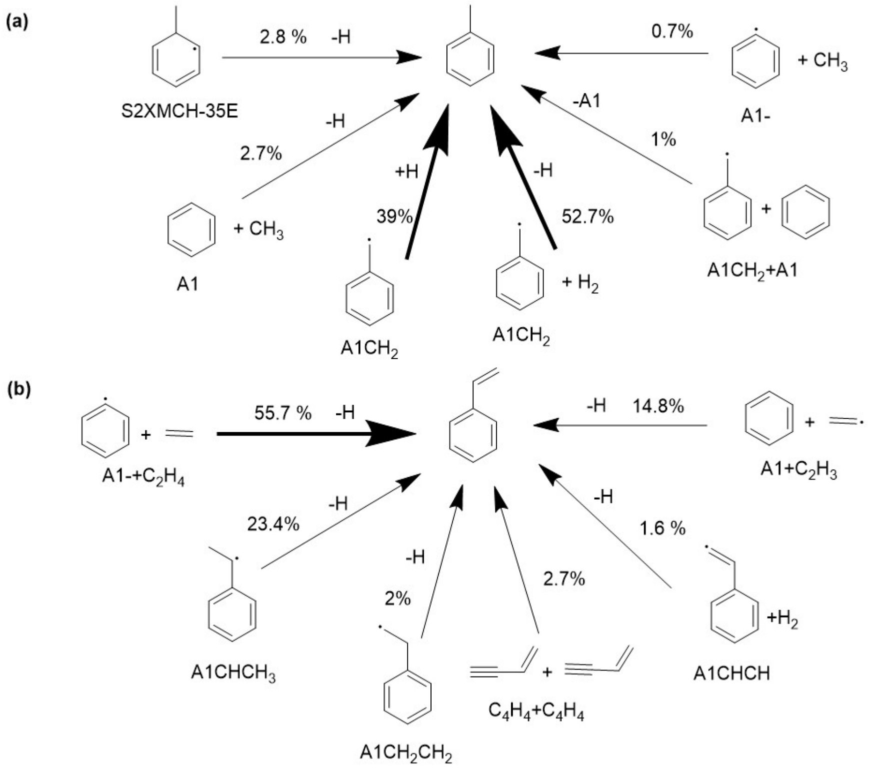

Figure 4.41: Reaction pathways analysis for formations of (a) toluene and (b) styrene in 135TCH pyrolysis at 1482 K with 85% conversion of 135TCH.

The dominant source of toluene is the association of H-atom with primary toluene radical ($A1CH_2$) from the various H atom sources (H atom (39%), H_2(52.7%), and A1 (1%)). H-loss of methycyclohexadienyl (S2XMCH-35E) radical is one of the minor toluene formation routes (2.8%). As shown in previous section (4.3.1.6), step-wise dehydrogenation/ dealkylation of cyclic intermediates are the sources of cyclohexadienyl radical. CH_3 radical addition with benzene (2.7%) and phenyl radical (0.7%) are the other minor toluene formation routes. Styrene is produced from multiple channels. The dominant channel of styrene formation is the addition of ethene with benzene radical (55.7%). H elimination from $A1CHCH_3$ also has major contribution (23.4%). Addition of ethene radical with benzene is also an important route of styrene formation (14.8%). H elimination from $A1CH_3CH_2$ has minor contribution (2%) on styrene formation. Other routes of styrene formation are the H_2 addition in A1CHCH (1.6%) and the addition of two C_4H_4 (2.7%).

Figure 4.42 shows the sensitivity analysis for toluene and styrene.

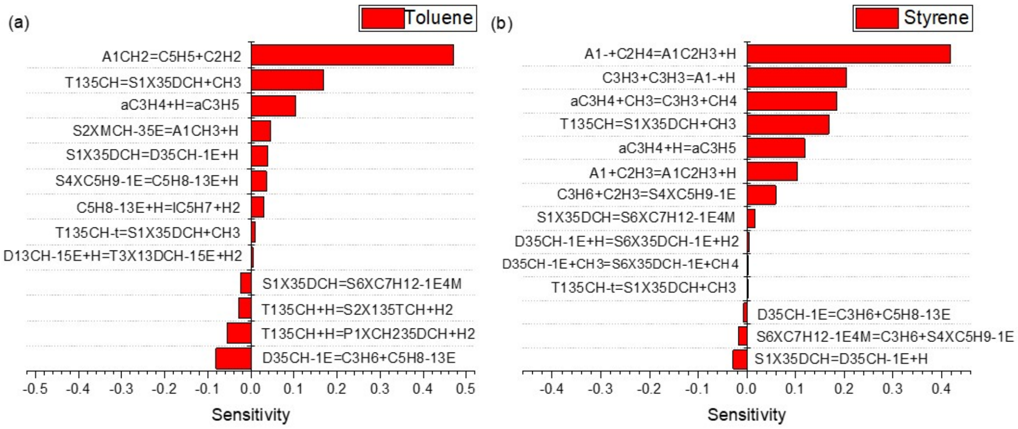

Figure 4.42: Normalized sensitivity analysis of (a) toluene and (b) styrene at 1482 K temperature with approximately 85% 135TCH conversion.

Dissociation of $A1CH_2$ into C_5H_5 and C_2H_2 is the most sensitive reaction and had positive effect on toluene formation. Formation of S1X35DCH by CH_3 elimination of T135CH has also the positive effect on toluene formation. Ring-opening off S1X35DCH has the negative effect on toluene formation. Allene (aC_3H_4) plays a role in toluene formation, its addition to H has a positive effect on toluene formation. Formation of dimethylcyclohexene (D35CH-1E) by H elimination has positive effect on toluene formation. On the other hand, dissociation of D35CH-1E has a negative effect on toluene formation. H-abstraction reaction of T135CH leads to secondary (S2X135TCH) and primary radical (P1X135TCH) and has the negative effect on toluene formation.

Addition of ethene (C_2H_4) with benzene radical (A1-) is the most sensitive reaction followed by addition of two propagyl radicals (C_3H_3) and both have positive effect on styrene formation. Allene also play a role on styrene formation. Its addition reaction with H and CH_3 has the positive effect on styrene formation. Like in benzene and toluene formations, S1X35DCH also plays a crucial role in styrene formation. Formation of S1X35DCH by CH_3 elimination of T135CH has the positive effect on styrene formation and the $\beta - C - H$ scission of S1X35DCH (S1X35DCH =D35CH-1E+H) had the negative effect on styrene formation. Addition of benzene as well as the addition of propene with ethene radical are the other important sensitive reactions and have positive effect on styrene formation.

In summary, step-wise dehydrogenation/dealkylation has no effect on benzene formation and is mainly formed by the addition of resonance stabilized radical like aC_3H_4, pC_3H_4, C_3H_3 etc. aC_3H_4 plays a critical role in the formation of all aromatic products. Its addition with H atom/CH_3 radical has the positive effect on the formation of all aromatic products. S1X35DCH is the other important radical which plays key role in aromatic formation. S1X35DCH formation by unimolecular decomposition of T135CH has positive effect on aromatic formation whereas as its ring-opening isomerization has the negetive effect on aromatic formation.

4.3.5 Rate constant of overall decomposition of 135TCH

The rate coefficient for the overall thermal decomposition of 135TCH (84%

T135CH and 16% T135CH-t) in the temperature range between 1119 K and 1529 K is determined using the following equation:

$$k = -\frac{1}{t} \ln \frac{[135TCH]_t}{[135TCH]_0} \tag{4.2}$$

Here t is the reaction time (dwell time), $[135TCH]_0$ is the initial concentration of 135TCH and $[135TCH]_t$ is the concentration of 135TCH after time t.

The rate constant expression which was obtained by linear fitting the data in figure 4.43:

$$k/s^{-1} = 10^{6.32\pm0.23} \exp^{\frac{(-25.1\pm1.3/kcal.mol^{-1})}{RT}} \tag{4.3}$$

4.3.6 Comparison with methylcyclohexane (MCH) and Isopropylcyclohexane (IPCH)

To understand the effect of multiple side-chain CH_3 group in overall decomposition we compare our results with pyrolysis of IPCH and pyrolysis of methylcyclohexane (experimental work of Liska et al.[9] on the high temperature, high pressure pyrolysis of methylcyclohexane using shock tube, from which we take the experimental

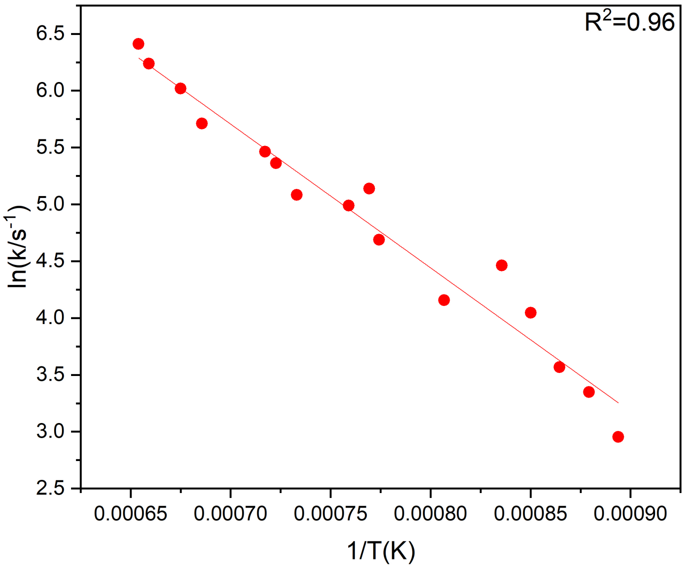

Figure 4.43: Arrhenius plot of overall decomposition of 135TCH.

results at 40 bar nominal pressure as that pressure is the close to our experimental pressure).

Both MCH and 135TCH start dissociating around 1100 K whereas IPCH starts dissociating at 1050K. Among the products from pyrolysis, both 135TCH and IPCH produce many branched species which are absent during MCH pyrolysis. The pyrolysis of 135TCH/IPCH produces branched unsaturated species like, methylpentadiene, methylbutadiene, methylcyclopentadiene which have not been reported during the pyrolysis of MCH.

The comparison of products formation of 135TCH and MCH is done at 1299 K and 1505 K. The results are shown in figure 4.44. Methane formation is high for 135TCH than IPCH and MCH which is expected as 135TCH has three side-chain CH_3 group. Formation of ethene is quite high for IPCH and MCH compared to 135TCH. Formation of acetylene is also quite high for MCH compared to 135TCH and IPCH. At high temperature 135TCH produces more amount of ethane than MCH but less than that of IPCH, whereas at low temperature 135TCH produces less ethane than MCH (but more than IPCH). Formation of propene is high for 135TCH pyrolysis compared to IPCH and MCH pyrolysis. Resonance stabilized intermediates like allene, propyne, and vinylacetylene are formed less in amount during 135TCH compared to MCH pyrolysis, whereas it is formed in more amount compared to IPCH pyrolysis. Formation of 1,3-butadiene is more during IPCH pyrolysis than 135TCH pyrolysis. Those resonance stabilized radicals are important precursors for the formation of aromatic intermediates like benzene, toluene, styrene. Formation of cyclopentadiene is more for 135TCH pyrolysis than that of IPCH and MCH pyrolysis.

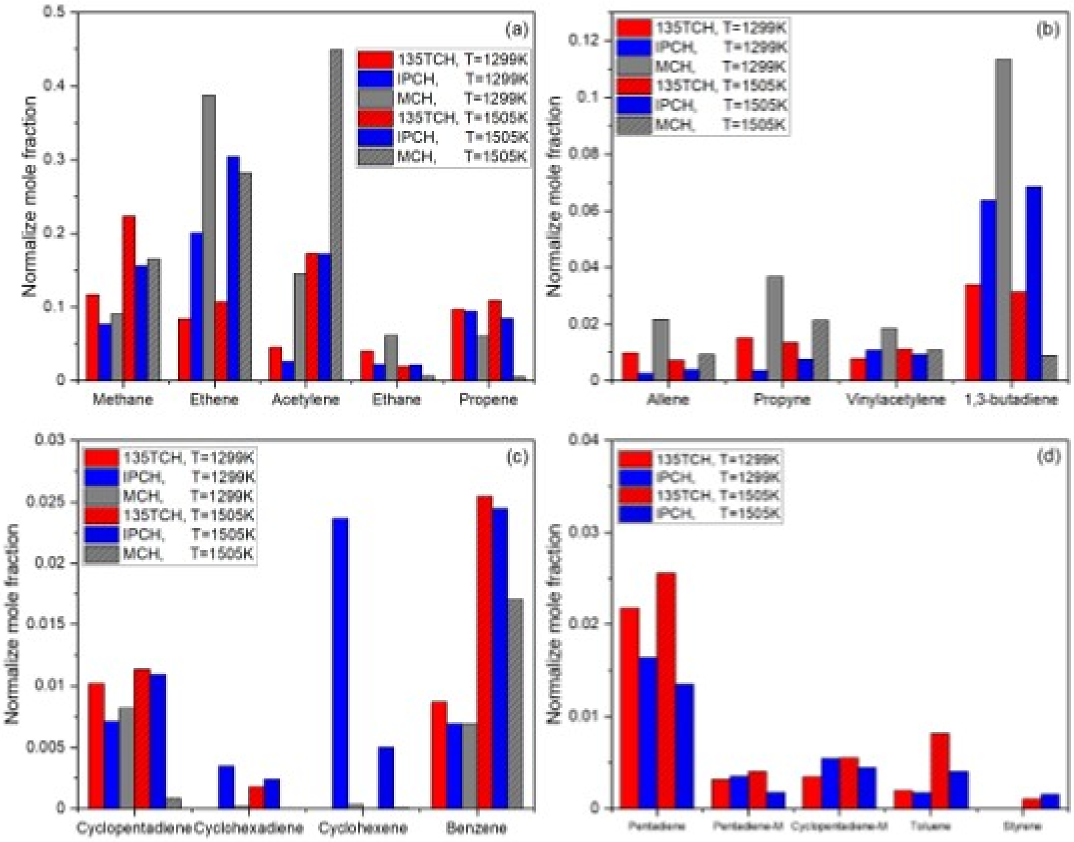

Figure 4.44: Comparisons of normalized mole fraction of (a) methane, ethane, acetylene, ethane, propene; (b) allene, propyne, vinylacetylene, 1,3-butadiene; (c) cyclopentadiene (C_5H_6), cyclohexadiene ($cC_6H_8 - 13E$), cyclohexene, benzene, (d) pentadiene, methylpentadiene (pentadiene-M), methylcyclopentadiene (cyclopentadiene-M), toluene and styrene from the experimental results of 135TCH (red column), IPCH (blue column) and MCH (grey column) at 1299 K (plane column) and 1505K (column with cross mark).

Amount of benzene formation is more during 135TCH pyrolysis than that from IPCH and MCH at high temperature. Formation of cyclohexadiene is very less during 135TCH compared to IPCH. Cyclohexene is not formed during 135TCH

pyrolysis. Toluene, styrene, pentadiene, methylpentadiene and methylcyclopentadiene are observed during 135TCH and IPCH pyrolyses which are not formed during MCH pyrolysis. At high temperature, formations of toluene, pentadiene, methylpentadiene and methylcyclopentadiene are more during 135TCH pyrolysis compared to IPCH whereas formation of styrene is slightly high for IPCH pyrolysis.
The first aromatic ring formation is considered as the rate controlling step to form polycyclic aromatic hydrocarbons and soot. As mentioned above, 135TCH pyrolysis produces little high amount of benzene compared to IPCH. But if we compare the benzene formation pathways of 135TCH and IPCH, we could see that those are not exactly same. ROP reveals that step-wise dehydration of cyclohexane has important contribution in benzene formation for IPCH (around10%) whereas it has no contribution for 135TCH. Isomerization of fulvene has a minor contribution in benzene formation for IPCH whereas it is one of the major pathways in benzene formation for 135TCH. Sensitivity analysis reveals that cyclohexyl radical plays the most important role in aromatic formation for IPCH whereas as allene plays the most important role in aromatic formation during 135TCH pyrolysis. There are few similarities also between 135TCH and IPCH pyrolysis on aromatics formations. Unimolecular decomposition reaction has always positive effects on aromatic formation whereas most of the H-abstraction reaction has negative effect (mostly abstraction at side-chain alkyl group) on aromatic formation. Ring-opening of alkylcyclohexane radical has negative effect on aromatic formation whereas H/CH3/other alkyl group elimination of it leads to alkylcyclohexene/cyclohexene has negative effect on it. Reverse DA reaction of alkylcyclohexene is also important in aromatic formation and it has negative effect. From these data, we can see that not only initial decomposition of alkylcyclohexane (ring-opening isomerization & side-chain alkyl group dissociation), H-abstraction reaction of alkylcyclohexane also plays an important role in aromatic formation. ROP reveals that initial consumption of IPCH is associated with 24.5% unimolecular decomposition, 74.1% H-abstraction and 1.2% ring-opening isomerization whereas initial consumption of 135TCH (cis isomer) is associated with 31.6% unimolecular decomposition, 64.7% H-abstraction and 2.3% ring-opening isomerization. As a result, 135TCH has little higher tendency of aromatic formation than IPCH.

4.4 Conclusion

In the present chapter, we investigated thermal decomposition/pyrolysis of 135TCH both theoritically and experimentally.

Thoeoritcal study shows the following conlusion:

(i)The pyrolysis mechanism of 135TCH includes
unimolecular decomposition and isomerization,

H-atom abstraction,

dissociation of alkene and alkyl-cyclohexene,

decomposition and isomerization of alkyl-cyclohexane radicals, and

stepwise dehydrogenation of cyclic intermediate.

(ii)The initial step of thermal decomposition of 135TCH is the side-chain C-C bond decomposition channel instead of the ring-opening isomerization channel. CH_3 elimination of T135CH-t is energetically favourable compared to the CH_3 elimination of T135CH.

(iii)Ring opening of T135CH-t has high energy barrier than that of T135CH.

(iv)Rate constant of CH_3 elimination of T135CH is less compared to MCH whereas as rate constant of CH_3 elimination of T135CH-t is higher than MCH.

(v)Rate constant of H-abstraction reaction for T135CH is higher than both T135CH-t and MCH.

(vi)Except primary cyclohexane radicals, ring-opening isomerization of 135TCH radical is associated with less energy barrier compared to that in MCH.

(vii)Alkenyl radicals formed from ring-opening of 135TCH radicals can either isomerize to cyclopentane radical (energetically most favourable) or isomerize to other alkenyl radicals by intramolecular H-migration or dissociate via β-scission.

(viii)Cyclopentadiene, methylcyclopentadiene, benzene, toluene are formed by stepwise dehydrogenation of cyclic intermediates. Stepwise dehydrogenation of 135TCH are energetically favourable than that of similar stepwise dehydrogenation of cyclohexene.

(ix)Small hydrocarbons like methane, ethylene, propylene, butadiene, pentadiene etc., are also formed as a final product of 135TCH.

Experimentally, we have investigated the pyrolysis of 135TCH (84%T135CH and 16%T135CH-t) by measuring species distribution from shock tube pyrolysis at the temperature range of 1017-1542 K and pressure ranging of 13.4–23.5 bar. A kinetic model for 135TCH has been built which includes 302 species and 967 reactions. The kinetic model has been validated against our experimental data. In general, the kinetic model gives good predictions against the experimental data. Methane, ethene, acetylene, ethane, propene, allene, propyne, 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, cyclopentadiene, and benzene are the major products of pyrolysis. Methane is the most abundant product at high temperature followed by acetylene. Benzene is the most abundant aromatic product followed by toluene and styrene which are present in little amount. 135TCH starts dissociation around 1110 K which is similar to the decomposition of MCH. ROP study reveals that CH_3 elimination reaction channel has strong effect on the unimolecular dissociation of 135TCH and is the most sensitive reaction of 135TCH consumption. Apart from CH_3 elimination channel of decomposition of 135TCH, the contribution of the H-abstraction reactions are significant in 135TCH consumption. Presence of multiple side-chain on the cyclohexene ring makes 135TCH to produce branched unsaturated species like, methylpentadiene, methylbutadiene, and methylcyclopentadiene. ROP analysis of the formation of the aromatic products reveals that step-wise dehydrogenation/ dealkylation of cyclic intermediate (cyclohexadiene radical) has no effect on benzene formation. Benzene is mainly formed by the addition of resonance stabilized radical/intermediates (C_3H_3, aC_4H_4, pC_3H_4, C_4H_6 etc) as well as from fulvene. Sensitivity analyses illustrate that allene (aC_3H_4) and dimethylcyclohexane radical (S1X35DCH) play key roles in the formations of aromatic products (benzene, toluene, and styrene). H/CH_3 addition with aC_3H_4 has positive effect on aromatic formation. Formation of S1X35DCH by CH_3 elimination of T134CH has positive effect on aromatic formation whereas its isomerization via ring-opening (S1X35DCH=S6XC7H12-1E4M) has the negative effect on aromatic formation.The rate of overall decomposition of 135TCH has been calculated and expressed in the equation 4.3.

135TCH exhibits comprehensive fuel characters as its pyrolytic intermediate could cover various hydrocarbons (saturated, unsaturated, branched unsaturated), aromatic (benzene, toluene, styrene) products which has been nominated as a surrogate fuel of RP-3[3]. This study is the first shock-tube as well as high pressure pyrolysis study of 135TCH and we present a detailed mechanism based on the theoretical calculations. This study will help to understand the unimolecular decomposition pathways and the reaction mechanism for aromatic products formation of multiple side-chain alkylcyclohexane.

Reference

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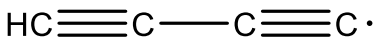
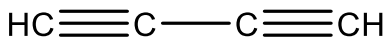
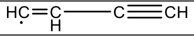
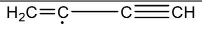
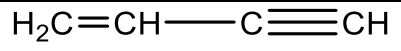
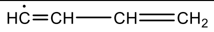
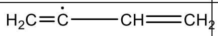
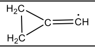
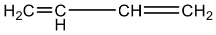
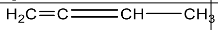
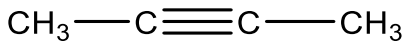
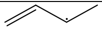
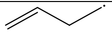
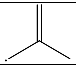
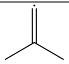
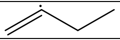
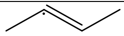
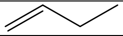
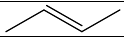
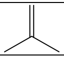
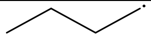
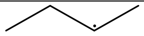
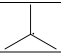
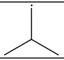
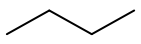
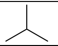
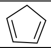
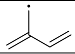
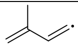
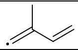
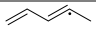
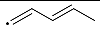
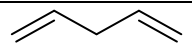
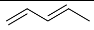
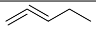
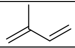
4.5 Additional Information

4.5.1 Nomenclature and structure of the species in the mechanism

Structure and nomenclature of the species used in the mechanism are given here.

formula	nomenclature	structure	formula	nomenclature	structure
C_4H	C4H	 $HC\equiv C-C\equiv C\cdot$	C_4H_2	C4H2	 $HC\equiv C-C\equiv CH$
C_4H_3	nC4H3	 $\underset{\cdot}{HC}=\underset{H}{C}-C\equiv CH$	C_4H_3	iC4H3	 $H_2C=\underset{\cdot}{C}-C\equiv CH$
C_4H_4	C4H4	 $H_2C=CH-C\equiv CH$	C_4H_5	nC4H5	 $H\dot{C}=CH-CH=CH_2$
C_4H_5	iC4H5	 $H_2C=\dot{C}-CH=CH_2$	C_4H_5	C4H5-2	 $CH_3-C\equiv C-\dot{C}H_2$
C_4H_5	c-C4H5		C_4H_6	C4H6	 $H_2C=\underset{H}{C}-CH=CH_2$
C_4H_6	C4H612	 $H_2C=C=CH-CH_3$	C_4H_6	C4H6-2	 $CH_3-C\equiv C-CH_3$
C_4H_7	SAXC4H7		C_4H_7	C4H7	
C_4H_7	iC4H7		C_4H_7	iC4H7-1	
C_4H_7	C4H7-2		C_4H_7	CH3CCHCH3	
C_4H_8	C4H8-1		C_4H_8	C4H8-2	
C_4H_8	iC4H8		C_4H_9	pC4H9	
C_4H_9	sC4H9		C_4H_9	tC4H9	
C_4H_9	iC4H9		C_4H_{10}	C4H10	
C_4H_{10}	iC4H10				
C_5H_5	C5H5		C_5H_6	C5H6	
C_5H_7	lC5H7		C_5H_7	P1XCH2C4H5-13E	
C_5H_7	S4XC4H4-13E2M		C_5H_7	S1XC4H4-13E2M	
C_5H_7	T4XC5H7-13E		C_5H_7	S1XC5H7-13E	
C_5H_8	C5H8-14E		C_5H_8	C5H8-13E	
C_5H_8	C5H8-12E		C_5H_8	C4H5-13E2M	
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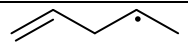
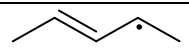
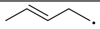
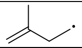
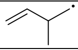
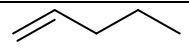
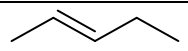
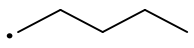
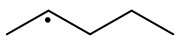
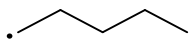
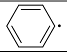
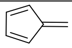
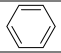
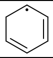
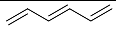
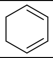
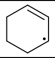
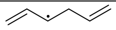
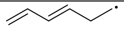
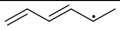
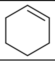
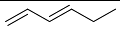
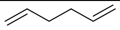
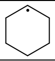
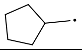
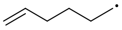
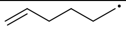
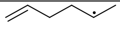
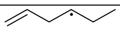
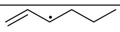
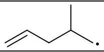
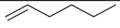
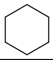
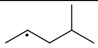
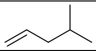
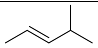
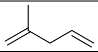
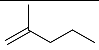
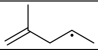
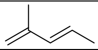
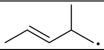
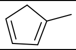
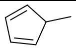
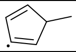
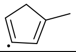
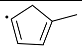
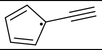
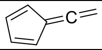
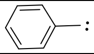
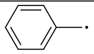
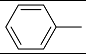
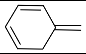
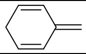
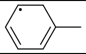
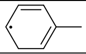
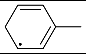
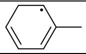
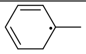
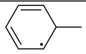
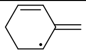
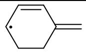
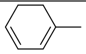
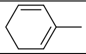
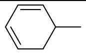
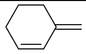
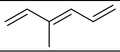
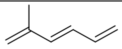
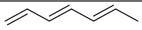
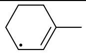
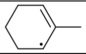
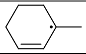
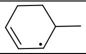
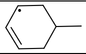
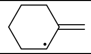
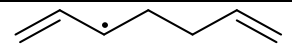
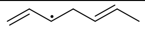
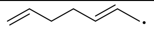
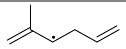
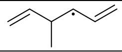
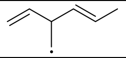
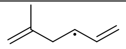
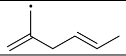
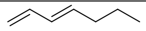
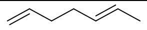
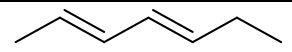
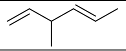
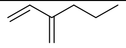
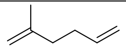
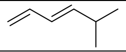
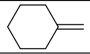
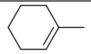
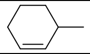
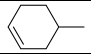
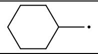
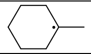
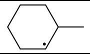
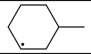
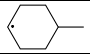
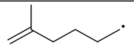
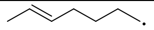
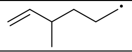
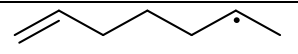
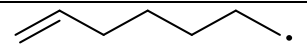
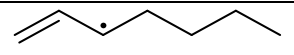
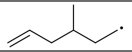
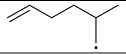
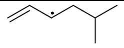
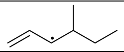
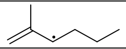
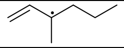
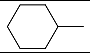
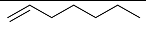
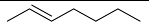
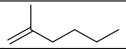
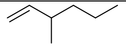
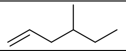
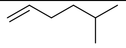
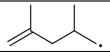
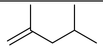
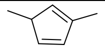
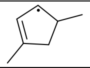
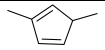
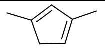
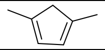
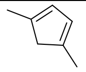
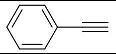
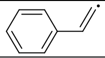
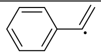
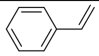
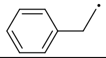
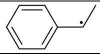
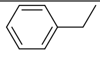
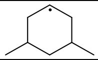
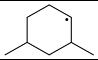
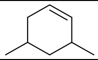
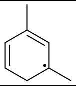
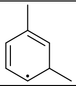
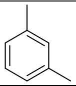
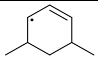
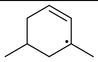
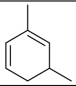
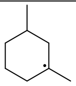
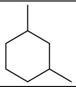
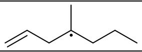
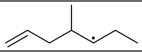
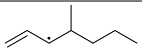
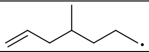
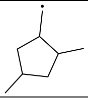
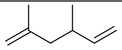
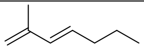
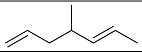
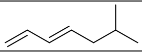
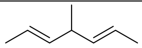
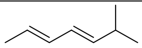
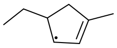
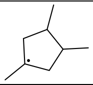
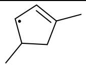
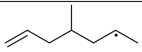
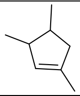
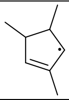
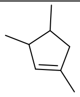
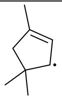
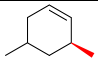
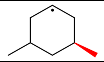
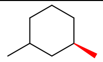
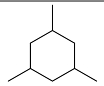
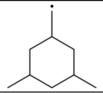
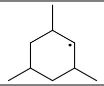
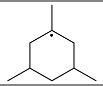
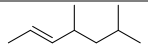
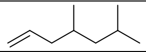
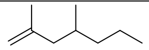
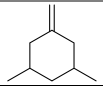
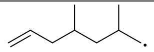
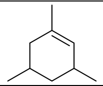
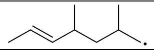
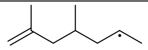
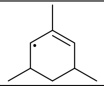
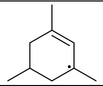
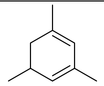
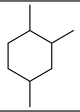
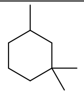
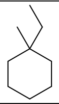
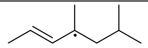
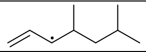
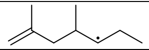
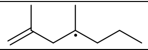
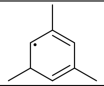
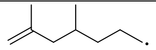
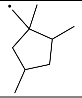
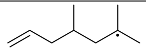
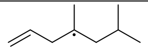
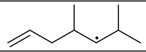
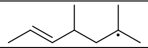
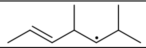
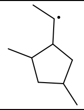
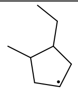
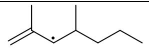
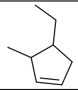
C_5H_9	S4XC5H9-1E		C_5H_9	S4XC5H9-2E	
C_5H_9	P5XC5H9-2E		C_5H_9	P4XC4H6-1E2M	
C_5H_9	P4XC4H6-1E3M		C_5H_{10}	C5H10-1E	
C_5H_{10}	C5H10-2E		C_5H_{11}	PXC5H11	
C_5H_{10}	S2XC5H11		C_5H_{11}	S3XC5H11	
C_6H_5	nC6H5		C_6H_5	A1-	
C_6H_6	fulvene		C_6H_6	A1	
C_6H_7	S1XcC6H7-24E		C_6H_8	C6H8-135E	
C_6H_8	cC6H8-13E		C_6H_9	S3XcC6H9-1E	
C_6H_9	S3XC6H9-15E		C_6H_9	P1XC6H9-13E	

C_6H_9	S2XC6H9-13E		C_6H_{10}	cC6H10	
			C_6H_{10}	C6H10-13E	
C_6H_{10}	C6H10-15E		C_6H_{11}	cC6H11	
C_6H_{11}	P1XCH2cC5H9		C_6H_{11}	S3XcC5H81M	
C_6H_{11}	P1XC6H11-1E		C_6H_{11}	S5XC6H11-1E	
C_6H_{11}	S4XC6H11-1E		C_6H_{11}	S3XC6H11-1E	
C_6H_{11}	P5XC5H8-1E4M		C_6H_{12}	C6H12-1E	
C_6H_{12}	cC6H12		C_6H_{13}	S2XC5H102M	
C_6H_{12}	C5H9-1E4M		C_6H_{12}	C5H9-2E4M	
C_6H_{10}	C5H7-14E2M		C_6H_{12}	C5H9-1E2M	
C_6H_{11}	S4XC5H8-1E2M		C_6H_{10}	C5H7-13E2M	
C_6H_{11}	P5XC5H8-2E4M		C_6H_8	cC5H5-13E1M	
C_6H_8	cC5H5-13E5M		C_6H_7	T2XcC5H4-13E5M	
C_6H_7	T3XcC5H4-13E1M		C_6H_7	T4XcC5H4-13E1M	
C_7H_5	C7H5		C_7H_6	C7H6	
C_7H_6	A1CH				
C_7H_7	A1CH2		C_7H_8	A1CH3	
C_7H_8	CH2cC6H6-35E		C_7H_8	CH2cC6H6-25E	
C_7H_9	S5XMCH-13E		C_7H_9	S4XMCH-15E	
C_7H_9	S3XMCH-15E		C_7H_9	S6XMCH-13E	
C_7H_9	T1XMCH-35E		C_7H_9	S2XMCH-35E	
C_7H_9	CH2S2XcC6H7-5E		C_7H_9	CH2S4XcC6H7-5E	
C_7H_{10}	MCH-13E		C_7H_{10}	MCH-15E	
C_7H_{10}	MCH-35E		C_7H_{10}	CH2cC6H8-2E	
C_7H_{10}	C6H7-135E3M		C_7H_{10}	C6H7-135E2M	
C_7H_{10}	C7H10-135E		C_7H_{11}	S3XMCH-1E	
C_7H_{11}	S2XMCH-5E		C_7H_{11}	T1XMCH-2E	
C_7H_{11}	S2XMCH-3E		C_7H_{11}	S5XMCH-3E	

C_7H_{11}	CH2S2XcC6H9		C_7H_{11}	S3XC7H11-16E	
C_7H_{11}	S3XC7H11-15E		C_7H_{11}	S4XC7H11-15E	
C_7H_{11}	P7XC7H11-15E			T1XC6H8-15E3M	
C_7H_{11}	S3XC6H8-15E2M		C_7H_{11}	S4XC6H8-15E3M	
C_7H_{11}	P1XCH2-3C6H9-15E		C_7H_{11}	S4XC6H8-15E2M	
C_7H_{11}	P1XCH2C6H9-15E		C_7H_{12}	C7H12-13E	
C_7H_{12}	C7H12-15E		C_7H_{12}	C7H12-24E	
C_7H_{12}	C6H9-15E3M		C_7H_{12}	CH2-3-C6H10-E	
C_7H_{12}	C6H9-15E2M		C_7H_{12}	C6H9-13E5M	
C_7H_{12}	CH2cC6H10		C_7H_{12}	MCH-1E	
C_7H_{12}	MCH-2E		C_7H_{12}	MCH-3E	
C_7H_{13}	PXCH2cC6H11		C_7H_{13}	T1XMCH	
C_7H_{13}	S2XMCH		C_7H_{13}	S3XMCH	
C_7H_{13}	S4XMCH		C_7H_{13}	P6XC6H10-1E2M	
C_7H_{13}	P7XC7H13-2E		C_7H_{13}	P6XC6H10-1E3M	
C_7H_{13}	S6XC7H13-1E		C_7H_{13}	P7XC7H13-1E	
C_7H_{13}	S3XC7H13-1E		C_7H_{13}	P6XC6H10-1E4M	
	P1XCH2C6H11-1E		C_7H_{13}	S3XC6H10-1E5M	
C_7H_{13}	S4XC7H13-2E		C_7H_{13}	S3XC6H10-1E4M	
C_7H_{13}	S3XC6H10-1E2M		C_7H_{13}	T3XC6H10-1E3M	
C_7H_{14}	MCH		C_7H_{14}	C7H14-1E	
C_7H_{14}	C7H14-2E		C_7H_{14}	C6H11-1E2M	
C_7H_{14}	C6H11-1E3M		C_7H_{14}	C6H11-1E4M	
C_7H_{14}	C6H11-1E5M		C_7H_{13}	P5XC5H7-1E24M	
C_7H_{14}	C5H8-1E24M		C_7H_{10}	cC5H4-13E25M	
C_7H_{11}	S5XcC5H5-3E13M		C_7H_{10}	cC5H4-13E35M	
C_7H_{10}	cC5H4-13E13M		C_7H_{10}	cC5H4-13E14M	
C_7H_{12}	C5H6-14E24M				

			C_8H_6	A1C2H	
C_8H_7	A1CHCH		C_8H_7	A1CCH2	
C_8H_8	A1C2H3		C_8H_9	A1CH2CH2	
C_8H_9	A1CHCH3				
C_8H_{10}	A1C2H5		C_8H_{15}	S1X35DCH	
C_8H_{15}	S2X35DCH		C_8H_{14}	D35CH-1E	
C_8H_{11}	T3X13DCH-15E		C_8H_{11}	S4X13DCH-15E	
C_8H_{10}	m-xylene		C_8H_{13}	S6X35DCH-1E	
C_8H_{13}	T3X35DCH-1E		C_8H_{12}	D13CH-15E	
C_8H_{15}	T3X13DCH		C_8H_{16}	D13CH	
C_8H_{15}	T4XC7H12-1E4M		C_8H_{15}	S5XC7H12-1E4M	
C_8H_{15}	S3XC7H12-1E4M		C_8H_{15}	P7XC7H12-1E4M	
C_8H_{15}	P1XCH2cC5H724M		C_8H_{14}	C6H8-15E24M	
C_8H_{14}	C7H11-13E2M		C_8H_{14}	C7H11-15E4M	
C_8H_{14}	C7H11-13E6M		C_8H_{14}	C7H11-25E4M	
C_8H_{14}	C7H11-24E6M		C_8H_{13}	S5XcC5H5-3E3M1Et	
C_8H_{15}	T4XcC5H6124M		C_8H_{15}	S5XC6H9-1E24M	
C_8H_{15}	S6XC7H12-1E4M		C_8H_{14}	cC5H5-3E135M	
C_8H_{13}	S2XcC5H4-3E135M		C_8H_{13}	T5XcC5H4-3E135M	
C_8H_{13}	S3XcC5H4-1E144M		C_8H_{14}	D35CH-1E-t	

C_8H_{15}	S1X35DCH-t		C_8H_{16}	D13CH-t	
C_9H_{18}	T135CH		C_9H_{17}	P1XCH235DCH	
C_9H_{17}	S2X135TCH		C_9H_{17}	T1X135TCH	
C_9H_{18}	C7H12-2E46M-t		C_9H_{18}	C7H12-1E46M	
C_9H_{18}	C7H12-1E24M		C_9H_{16}	CH2-35DCH	
C_9H_{17}	P7XC7H11-1E46M		C_9H_{16}	T135CH-1E	
C_9H_{17}	P7XC7H11-2E46M-t		C_9H_{17}	S6XC7H11-1E24M	
C_9H_{15}	S6X135TCH-1E		C_9H_{15}	T3X135TCH-1E	
C_9H_{14}	T135CH-13E		C_9H_{18}	T124CH	
C_9H_{18}	T133CH		C_9H_{18}	MEtCH	
C_9H_{17}	T4XC7H11-2E46M-t		C_9H_{17}	S3XC7H11-1E46M	
C_9H_{17}	S5XC7H11-1E24M		C_9H_{17}	T4XC7H11-1E24M	
C_9H_{13}	S6X135TCH-13E		C_9H_{17}	P7XC7H11-1E24M	
C_9H_{17}	P1XCH2cC5H6124M		C_9H_{17}	T6XC7H11-1E46M	
C_9H_{17}	T4XC7H11-1E46M		C_9H_{17}	S5XC7H11-1E46M	
C_9H_{17}	T6XC7H11-2E46M-t		C_9H_{17}	S5XC7H11-2E46M-t	
C_9H_{17}	S2XC2H4cC5H735M		C_9H_{17}	T3XcC5H635M1Et	
C_9H_{17}	S3XC7H11-1E24M		C_9H_{16}	cC5H5-3E35M1Et	

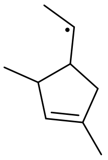
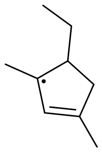
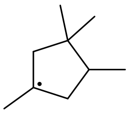
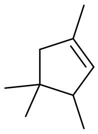
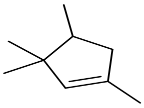
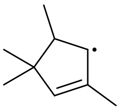
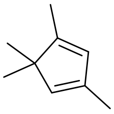
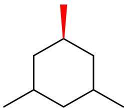
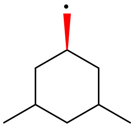
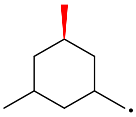
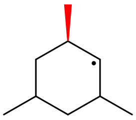
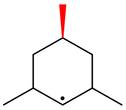
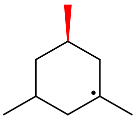
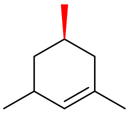
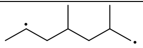
C_9H_{15}	S2XcC5H4-3E35MEt		C_9H_{15}	T5XcC5H4-3E35MEt	
C_9H_{17}	T4XcC5H51124M		C_9H_{16}	cC5H4-1E1344M	
C_9H_{16}	cC5H4-3E1355M		C_9H_{15}	S2XcC5H3-3E1355M	
C_9H_{14}	cC5H2-13E1355M		C_9H_{18}	T135CH-t	
C_9H_{17}	P1XCH235DCH-t		C_9H_{17}	P3XCH235DCH-t	
C_9H_{17}	S2X135TCH-t		C_9H_{17}	S4X135TCH-t	
C_9H_{17}	T3X135TCH-t		C_9H_{16}	T135CH-3E-t	
C_9H_{18}	T135CH-bi				

Figure 4.45: Nomenclature and structure of the species in the mechanism.

4.5.2 Mechanism

!**

!Reaction mechanism

ELEMENTS

H C AR END

SPECIES

AR H H2

C CH CH2 CH2* CH3 CH4

C2H C2H2 H2CC C2H3 C2H4 C2H5 C2H6

C3H2 C3H3 aC3H4 pC3H4 aC3H5 CH3CCH2 CH3CHCH C3H6 nC3H7 iC3H7 C3H8

C4H C4H2 nC4H3 iC4H3 C4H4 nC4H5 iC4H5 C4H5-2 c-C4H5 C4H6 C4H612 C4H6-2 SAXC4H7 C4H7 iC4H7 iC4H7-1 C4H7-2 CH3CCHCH3 C4H8-1 C4H8-2 iC4H8 pC4H9 sC4H9 tC4H9 iC4H9 C4H10 iC4H10

C5H2 C5H3 C5H4 cC5H4 lC5H5 C5H5 C5H6 lC5H7 P1XCH2C4H5-13E S4XC4H4-13E2M S1XC4H4-13E2M T4XC5H7-13E S1XC5H7-13E C5H8-14E C5H8-13E C5H8-12E C4H5-13E2M S3XC5H9-1E P5XC5H9-1E S4XC5H9-1E S4XC5H9-2E P5XC5H9-2E P4XC4H6-1E2M P4XC4H6-1E3M C5H10-1E C5H10-2E PXC5H11 S2XC5H11 S3XC5H11

C6H2 C6H3 l-C6H4 o-C6H4 nC6H5 A1- fulvene A1 S1XcC6H7-24E C6H8-135E cC6H8-13E S3XcC6H9-1E S3XC6H9-15E P1XC6H9-13E S2XC6H9-13E cC6H10 CH2cC5H8 C6H10-13E C6H10-15E cC6H11 P1XCH2cC5H9 S3XcC5H81M P1XC6H11-1E S5XC6H11-1E S4XC6H11-1E S3XC6H11-1E P5XC5H8-1E4M C6H12-1E cC6H12

S2XC5H102M C5H9-1E4M C5H9-2E4M C5H7-14E2M C5H9-1E2M S4XC5H8-1E2M C5H7-13E2M P5XC5H8-2E4M cC5H5-13E1M cC5H5-13E5M T2XcC5H4-13E5M T3XcC5H4-13E1M T4XcC5H4-13E1M

C7H5 C7H6 A1CH C6H4CH3 A1CH2 A1CH3 CH2cC6H6-35E CH2cC6H6-25E S5XMCH-13E S4XMCH-15E S3XMCH-15E S6XMCH-13E T1XMCH-35E S2XMCH-35E CH2S2XcC6H7-5E CH2S4XcC6H7-5E MCH-13E MCH-15E MCH-35E CH2cC6H8-2E C6H7-135E3M C6H7-135E2M C7H10-135E S3XMCH-1E S2XMCH-5E T1XMCH-2E S2XMCH-3E S5XMCH-3E CH2S2XcC6H9 S3XC7H11-16E S3XC7H11-15E S4XC7H11-15E P7XC7H11-15E T1XC6H8-15E3M S3XC6H8-15E2M S4XC6H8-15E3M P1XCH2-3C6H9-15E S4XC6H8-15E2M P1XCH2C6H9-15E C7H12-13E C7H12-15E C7H12-24E C6H9-15E3M CH2-3-C6H10-E C6H9-15E2M C6H9-13E5M CH2cC6H10 MCH-1E MCH-2E MCH-3E PXCH2cC6H11 T1XMCH S2XMCH S3XMCH S4XMCH P6XC6H10-1E2M P7XC7H13-2E P6XC6H10-1E3M S6XC7H13-1E P7XC7H13-1E S3XC7H13-1E P6XC6H10-1E4M P1XCH2C6H11-1E S3XC6H10-1E5M S4XC7H13-2E S3XC6H10-1E4M S3XC6H10-1E2M T3XC6H10-1E3M MCH C7H14-1E C7H14-2E C6H11-1E2M C6H11-1E3M C6H11-1E4M C6H11-1E5M

P5XC5H7-1E24M C5H8-1E24M cC5H4-13E25M S5XcC5H5-3E13M cC5H4-13E35M cC5H4-13E13M cC5H4-13E14M C5H6-14E24M

A1C2H- A1C2H* A1C2H A1CHCH A1CCH2 A1C2H3 A1CH2CH2 A1CHCH3 C6H4C2H4 A1C2H5

S1X35DCH S2X35DCH D35CH-1E T3X13DCH-15E S4X13DCH-15E m-xylene S6X35DCH-1E T3X35DCH-1E D13CH-15E T3X13DCH D13CH T4XC7H12-1E4M S5XC7H12-1E4M S3XC7H12-1E4M P7XC7H12-1E4M P1XCH2cC5H724M C6H8-15E24M C7H11-13E2M C7H11-15E4M C7H11-13E6M C7H11-25E4M C7H11-24E6M S5XcC5H5-3E3M1Et T4XcC5H6124M S5XC6H9-1E24M S6XC7H12-1E4M cC5H5-3E135M S2XcC5H4-3E135M T5XcC5H4-3E135M S3XcC5H4-1E144M D35CH-1E-t S1X35DCH-t D13CH-t

C9H7 C9H8

T135CH P1XCH235DCH S2X135TCH T1X135TCH C7H12-2E46M-t C7H12-1E46M C7H12-1E24M CH2-35DCH P7XC7H11-1E46M T135CH-1E P7XC7H11-2E46M-t S6XC7H11-1E24M S6X135TCH-1E T3X135TCH-1E T135CH-13E T124CH T133CH MEtCH T4XC7H11-2E46M-t S3XC7H11-1E46M S5XC7H11-1E24M T4XC7H11-1E24M S6X135TCH-13E P7XC7H11-1E24M P1XCH2cC5H6124M T6XC7H11-1E46M T4XC7H11-1E46M S5XC7H11-1E46M T6XC7H11-2E46M-t S5XC7H11-2E46M-t S2XC2H4cC5H735M T3XcC5H635M1Et S3XC7H11-1E24M cC5H5-3E35M1Et S2XcC5H4-3E35MEt T5XcC5H4-3E35MEt T4XcC5H51124M cC5H4-1E1344M cC5H4-3E1355M S2XcC5H3-3E1355M cC5H2-13E1355M T135CH-t

P1XCH235DCH-t P3XCH235DCH-t S2X135TCH-t S4X135TCH-t T3X135TCH-t T135CH-3E-t T135CH-bi

REACTIONS

! CH reactions

CH+H = C+H2 1.100E+14 0.000 0.00 ! GRI

CH+H2 = CH2+H 1.107E+08 1.790 1670.00 ! GRI

! CH2(triplet) reactions

CH2+H(+M) = CH3(+M) 2.500E+16 -0.800 0.00 ! GRI

LOW / 3.200E+27 -3.140 1230.00/

TROE/ 0.6800 78.00 1995.0 5590.0 /

H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/

CH2+H2 = H+CH3 5.000E+05 2.000 7230.00 ! GRI

CH2+C = C2H+H 5.000E+13 0.000 0.00 ! GRI

CH2+CH = C2H2+H 4.000E+13 0.000 0.00 ! GRI

CH2+CH2 = C2H2+H2 3.200E+13 0.000 0.00 ! GRI

! CH2(singlet) reactions

CH2*+AR = CH2+AR 9.000E+12 0.000 600.00 ! GRI

CH2*+H = CH+H2 3.000E+13 0.000 0.00 ! GRI

CH2*+H2 = CH3+H 7.000E+13 0.000 0.00 ! GRI

```
! CH3 reactions
CH3+H(+M) = CH4(+M) 1.270E+16 -0.630 383.00 ! GRI
LOW / 2.477E+33 -4.760 2440.00 /
TROE/ 0.7830 74.00 2941.00 6964.0 /
H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/
CH3+C = C2H2+H 5.000E+13 0.000 0.00 ! GRI
CH3+CH = C2H3+H 3.000E+13 0.000 0.00 ! GRI
CH3+CH2 = C2H4+H 4.000E+13 0.000 0.00 ! GRI
CH3+CH2* = C2H4+H 1.200E+13 0.000 -570.00 ! GRI
! CH3+CH3(+M) = C2H6(+M) 2.120E+16 -0.970 620.00 ! GRI !
! LOW / 1.770E+50 -9.670 6220.00/
! TROE/ 0.5325 151.0 1038.00 4970.0 /
! H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/
CH3+CH3 = H+C2H5 4.990E+12 0.100 10600.00 ! GRI
CH3+C2H = C3H3+H 2.41E+13 0.0 0.0 ! 1986 TSA/HAM
CH3+CH3(+M)=C2H6(+M) 3.6E13 0.000 0 !
LOW /1.269E41 -7.0 2762/ !
TROE /0.62 73 1180 1E30/ ! Fc=0.38exp(-T/73)+0.62exp(-T/1180)
! Baulch DL Bowman CT Cobos CJ Cox RA Just Th Kerr JA Pilling MJ Stocker D Troe J Tsang W Walker RW Warnatz J JPCRD 34:757-1397 2005
!CH4 reactions
CH4+H = CH3+H2 6.600E+08 1.620 10840.00 ! GRI
CH4+CH = C2H4+H 6.000E+13 0.000 0.00 ! GRI
CH4+CH2 = CH3+CH3 2.460E+06 2.000 8270.00 ! GRI
CH4+CH2* = CH3+CH3 1.600E+13 0.000 -570.00 ! GRI
CH4+C2H = C2H2+CH3 1.810E+12 0.0 500.0 ! 1986 TSA/HAM
DUPLICATE
!!!C2
! C2H reactions
C2H+H(+M) = C2H2(+M) 1.000E+17 -1.000 0.00 ! GRI
LOW / 3.750E+33 -4.800 1900.00/
TROE/ 0.6464 132.00 1315.00 5566.0/
H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/
C2H+H2 = H+C2H2 4.900E+05 2.500 560.00 ! GRI
DUPLICATE
C2H+H2=C2H2+H 4.1E05 2.390 864 !
DUPLICATE
! Harding LB Schatz GC Chiles RA JCP 76:5172-5173 1982 C2H+CH4=CH3+C2H2 7.2E12 0.000 976 !
DUPLICATE
```

! Opansky BJ Leone SR JPC 100:4888-4892 1996

! C2H2 reactions

C2H2 (+M) = H2CC (+M) 8.000E+14 -0.520 50750.00 ! 1999 Laskin&Wang

LOW / 2.450E+15 -0.640 49700.0/

H2/2.0/ CH4/2.0/ C2H6/3.0/

C2H2/2.5/ C2H4/2.5/

! C2H3 (+M) = C2H2+H (+M) 3.860E+08 1.620 37048.2 ! 1996 Knyazev&Slagle

! LOW / 2.565E+27 -3.400 35798.72/

! TROE/ 1.9816 5383.7 4.2932 -0.0795 /

! H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/

! C2H2/3.00/ C2H4/3.00/

C2H2+H(+M)=C2H3(+M) 1.7E10 1.266 2709 !

LOW /6.3E31 -4.664 3780 / !

TROE /0.7878 -10212 1.E-30 / !

H2/2/ !

! Miller JA Klippenstein PCCP 6:1192-1202 2004

! Vinylidene reactions

H2CC+H = C2H2+H 1.000E+14 0.000 0.00 ! USC Mech V2.0 Estimated

H2CC=C2H2 1.0E07 0.000 0 !

! JAM est

! C2H3 reactions

! C2H3+H(+M) = C2H4(+M) 6.080E+12 0.270 280.00 ! GRI1.2

! LOW / 1.400E+30 -3.860 3320.00/

! TROE/ 0.7820 207.50 2663.00 6095.00/

! H2/2.0/ CH4/2.0/ C2H6/3.0/

! AR/0.7/ C2H2/3.00/ C2H4/3.00/

! C2H3+H = C2H2+H2 9.000E+13 0.000 0.00 ! 1986 TSA/HAM

C2H3+H = H2CC+H2 6.000E+13 0.000 0.00 ! USC Mech V2.0 Estimated

! C2H3+CH3 = C2H2+CH4 3.920E+11 0.000 0.00 ! 1986 TSA/HAM

C2H3+C2H3 = C2H2+C2H4 9.600E+11 0.00 0. ! NIST Database

C2H3+H(+M)=C2H4(+M) 3.9E13 0.200 0 !

LOW /2.10E24 -1.3 0/ !

TROE /0.5 1E-30 1E30 1E30/ !

! Harding LB Georgievskii Y Klippenstein SJ JPCA 109:4646-4656 2005 ! Monks PS Nesbitt FL Payne WA Scanlon M Stief LJ Shallcross DE JPC 99:17151-17159 1995

C2H3+H=C2H2+H2 4.5E13 0.000 0 ! ! Monks PS Nesbitt FL Payne WA Scanlon M Stief LJ Shallcross DE JPC 99:17151-17159 1995

C2H3+CH3=C2H2+CH4 9.0E12 0.000 -765 ! ! Stoliarov SI Knyazev VD Slagle IR JPCA 104:9687-9697 2000

! C2H3+CH=CH2+C2H2 5.0E13 0.000 0 ! ! JAM est

C2H3+C2H=C2H2+C2H2 3.0E13 0.000 0 ! ! JAM est

! C2H4 reactions

! H+C2H4(+M)=C2H5(+M) 5.40E+11 0.45 1820. ! GRI3.0

! LOW / 6.00E+41 -7.62 6970./

! TROE / 0.9753 210 984 4374/

! H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/

C2H4(+M)=H2+C2H2(+M) 8.00E+12 0.44 88770. ! GRI3.0

LOW / 1.58E+51 -9.30 97800./

TROE / 0.7345 180 1035 5417/

H2/2.0/ CH4/2.0/ C2H6/3.0/

AR/0.7/

! C2H4+H = C2H3+H2 5.070E+07 1.900 12950.00 ! 1996 Knyazev et al.

C2H4+CH = aC3H4+H 3.000E+13 0.000 0.00 ! USC Mech V2.0 Estimated

C2H4+CH = pC3H4+H 3.000E+13 0.000 0.00 ! USC Mech V2.0 Estimated

C2H4+CH2 = aC3H5+H 2.000E+13 0.000 6000.00 ! USC Mech V2.0 Estimated

C2H4+CH2* = H2CC+CH4 5.000E+13 0.000 0.00 ! USC Mech V2.0 Estimated

C2H4+CH2* = aC3H5+H 5.000E+13 0.000 0.00 ! USC Mech V2.0 Estimated

! C2H4+CH3 = C2H3+CH4 2.270E+05 2.000 9200.00 ! GRI

C2H4+C2H = C4H4+H 1.200E+13 0.000 0.00 ! 1986 TSA/HAM

C2H4+H(+M)=C2H5(+M) 1.4E09 1.463 1355 !

LOW /2.0E39 -6.642 5769/ !

TROE /-0.569 299 9147 152.4/ ! ! Miller JA Klippenstein PCCP 6:1192-1202 2004 !

C2H4(+M)=H2CC+H2(+M) 8.0E12 0.440 88800 ! LOW/7.0E50 -9.31 99900/

TROE/0.735 180 1035 5417/

AR/0.7/

! Wang H IJCK 33:698-706 2001 !

C2H4+H=C2H3+H2 2.4E02 3.620 11266 !

! Baulch DL Bowman CT Cobos CJ Cox RA Just Th Kerr JA Pilling MJ Stocker D Troe J Tsang W Walker RW Warnatz J JPCRD 34:757-1397 2005

C2H4+CH3=C2H3+CH4 6.0E07 1.560 16630 !

! Baulch DL Bowman CT Cobos CJ Cox RA Just Th Kerr JA Pilling MJ Stocker D Troe J Tsang W Walker RW Warnatz J JPCRD 34:757-1397 2005

! C2H5 reactions

C2H5+H(+M) = C2H6(+M) 5.210E+17 -0.990 1580.00 ! GRI

LOW / 1.990E+41 -7.080 6685.00/

TROE / 0.8422 125.0 2219.00 6882.0/

H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/

C2H5+H = C2H4+H2 2.000E+12 0.000 0.00 ! GRI

C2H5+CH3(+M) = C3H8(+M) 4.90E+14 -0.50 0.0 ! 1988 TSA

LOW / 6.80E+61 -13.42 6000.0/

TROE / 1.000 1000.0 1433.9 5328.8 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C2H5+CH3=C2H4+CH4 9.0E11 0.000 0 !

! Baulch DL Bowman CT Cobos CJ Cox RA Just Th Kerr JA Pilling MJ Stocker D Troe J Tsang W Walker RW Warnatz J JPCRD 34:757-1397 2005 !

C2H5+C2H5=C2H6+C2H4 1.5E12 0.000 0 !

! Baulch DL Cobos CJ Cox RA Esser C Frank P Just Th Kerr JA Pilling MJ Troe J Walker RW Warnatz J JPCRD 21:403 1992 !

! C2H6 reactions

! C2H6+H = C2H5+H2 1.15E+08 1.900 7530.00 ! GRI

! C2H6+CH2* = C2H5+CH3 4.00E+13 0.000 -550.00 ! GRI

! C2H6+CH3 = C2H5+CH4 6.14E+06 1.740 10450.00 ! GRI

C2H6+C2H=C2H2+C2H5 3.61E+12 0.00 0 ! 1986 TSA/HAM

C2H6+C2H3=C2H4+C2H5 6.01E+02 3.30 10502 ! 1986 TSA/HAM

C2H6+H=C2H5+H2 9.8E13 0.000 9220 !

! Baulch DL Bowman CT Cobos CJ Cox RA Just Th Kerr JA Pilling MJ Stocker D Troe J Tsang W Walker RW Warnatz J JPCRD 34:757-1397 2005

C2H6+CH3=C2H5+CH4 5.6E10 0.000 9418 !

DUPLICATE !

C2H6+CH3=C2H5+CH4 8.4E14 0.000 22250 !

DUPLICATE !

! Baulch DL Bowman CT Cobos CJ Cox RA Just Th Kerr JA Pilling MJ Stocker D Troe J Tsang W Walker RW Warnatz J JPCRD 34:757-1397 2005 !

C2H6+CH2*=C2H5+CH3 1.2E14 0.000 0 ! ! Tsang W Hampson RF JPCRD 15:1087 1986 !

!!!C3

! C3H2 reactions

C3H2+H(+M)=C3H3(+M) 1.02e+13 0.27 279.64 ! 2009 Blanquart et al.

LOW/ 2.80e+30 -3.860 3319.79/

TROE/ 0.782 207.50 2663.00 6095.00/

H2/2.00/ AR/0.70/

CH4/2.00/ C2H6/3.00/

C3H2+CH=C4H2+H 5.00E+13 0.0 0. ! USC Mech V2.0

! C3H3 reactions

C3H3+H = C3H2+H2 1.00E+13 0.0 1000. ! USC Mech V2.0

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C2H2+CH2 = C3H3+H 1.20E+13 0.00 6620.00 ! 1988 Bohland et al.; 1988 Frank et al.
C2H2+CH2* = C3H3+H 2.00E+13 0.00 0.00 ! 1997 Wang&Frenklach
! C3H4 reactions
aC3H4=pC3H4 6.0256E+53 -12.18 84276. ! J. A. Miller Mechanism
PLOG /0.03947 6.0256E+53 -12.18 84276./
PLOG /1. 7.7625E+39 -7.80 78446./
PLOG /10. 4.7863E+48 -10.0 88685./
C3H3+H=pC3H4 3.6308E+36 -7.36 6039. ! J. A. Miller Mechanism
PLOG /0.03947 3.6308E+36 -7.36 6039./
PLOG /1. 7.943E+29 -5.06 4861./
PLOG /10. 1.072E24 -3.15 3261./
C3H3+H=aC3H4 3.3884E+36 -7.41 6337. ! J. A. Miller Mechanism
PLOG /0.03947 3.3884E+36 -7.41 6337./
PLOG /1. 3.1623E+29 -5. 4711./
PLOG /10. 8.7096E+23 -3.20 3255./
aC3H4+H = C3H3+H2 6.60E+03 3.1 5522 ! 2008 Miller 30 Torr
aC3H4+CH3=C3H3+CH4 6.600E-4 5.000 8300 ! 2009 Kiefer et al.
H+aC3H4 = H+pC3H4 1.47E+13 0.26 4103 ! 2008 Miller 30 Torr
aC3H4+C2H = C2H2+C3H3 1.00E+13 0.0 0.0 ! 1997 Wang&Frenklach
H+aC3H4 = CH3+C2H2 2.72E+09 1.2 6834 ! 2008 Miller 30 Torr
pC3H4+H = C3H3+H2 3.57E+04 2.8 4821 ! 2008 Miller 30 Torr
pC3H4+CH3=C3H3+CH4 2.200E-4 5.000 8300 ! 2009 Kiefer et al.
pC3H4+C3H3 = aC3H4+C3H3 6.14E+06 1.74 10450. ! USC Mech V2.0 Estimated
pC3H4+C2H = C2H2+C3H3 1.00E+13 0.0 0.0 ! USC Mech V2.0 Estimated
H+pC3H4 = C2H2+CH3 3.89E+10 0.989 4114 ! 2008 Miller 30 Torr
! CH3CHCH CH3CCH2 and aC3H5 reactions
CH3CHCH+H = aC3H5+H 1.47E+13 0.26 4103 ! Ref H+aC3H4=H+pC3H4
CH3CCH2+H = pC3H4+H2 3.34E+12 0.00 0.0 ! 1999 Davis et al.
CH3CCH2+H = aC3H5+H 1.47E+13 0.26 4103 ! Ref aC3H4+H=pC3H4+H
CH3CCH2+CH3 = pC3H4+CH4 1.00E+11 0.00 0.0 ! 1999 Davis et al.
aC3H5+H = aC3H4+H2 9.56E+03 2.80 3291.11 ! 2009 Blanquart et al.
aC3H5+CH3 = aC3H4+CH4 1.50E+12 -0.32 -131.0 ! 1991 TSA 3.00E+12/2
C2H5+C2H3 = aC3H5+CH3 8.00E+25 -3.46 11775.0 ! 1986 TSA/HAM RRKM 0.1 atm
aC3H4+H = CH3CHCH 1.10E+30 -6.52 15200.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 5.05E+29 -6.52 15200.0 / ! EST 0.1 atm /2
PLOG / 0.1 1.10E+30 -6.52 15200.0 /
PLOG / 1.0 5.40E+29 -6.09 16300.0 /
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PLOG / 10.0 2.60E+31 -6.23 18700.0 /
PLOG / 100.0 3.20E+31 -5.88 21500.0 /
pC3H4+H = CH3CHCH 1.00E+25 -5.00 1800.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 5.0E+24 -5.00 1800.0 / ! EST 0.1 atm /2
PLOG / 0.1 1.00E+25 -5.00 1800.0 /
PLOG / 1.0 5.50E+28 -5.74 4300.0 /
PLOG / 10.0 1.00E+34 -6.88 8900.0 /
PLOG / 100.0 9.70E+37 -7.63 13800.0 /
C2H2+CH3 = CH3CHCH 1.40E+32 -7.14 10000.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 7.0E+31 -7.14 10000.0 / ! EST 0.1 atm /2
PLOG / 0.1 1.40E+32 -7.14 10000.0 /
PLOG / 1.0 3.20E+35 -7.76 13300.0 /
PLOG / 10.0 2.40E+38 -8.21 17100.0 /
PLOG / 100.0 1.40E+39 -8.06 20200.0 /
aC3H4+H = CH3CCH2 9.20E+38 -8.65 7000.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 4.60E+38 -8.65 7000.0 / ! EST 0.1 atm /2
PLOG / 0.1 9.20E+38 -8.65 7000.0 /
PLOG / 1.0 9.46E+42 -9.43 11190.0 /
PLOG / 2.0 8.47E+43 -9.59 12462.0 /
PLOG / 5.0 6.98E+44 -9.70 14032.0 /
PLOG / 10.0 1.50E+45 -9.69 15100.0 /
PLOG / 100.0 1.80E+43 -8.78 16800.0 /
pC3H4+H = CH3CCH2 4.60E+44 -10.21 10200.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 2.30E+44 -10.21 10200.0 / ! EST 0.1 atm /2
PLOG / 0.1 4.60E+44 -10.21 10200.0 /
PLOG / 1.0 1.66E+47 -10.58 13690.0 /
PLOG / 2.0 5.04E+47 -10.61 14707.0 /
PLOG / 5.0 9.62E+47 -10.55 15910.0 /
PLOG / 10.0 7.00E+47 -10.40 16600.0 /
PLOG / 100.0 3.20E+44 -9.11 17400.0 /
C2H2+CH3 = CH3CCH2 6.80E+20 -4.16 18000.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 3.40E+20 -4.16 18000.0 / ! EST 0.1 atm /2
PLOG / 0.1 6.80E+20 -4.16 18000.0 /
PLOG / 1.0 4.99E+22 -4.39 18850.0 /
PLOG / 2.0 6.00E+23 -4.60 19571.0 /
PLOG / 5.0 7.31E+25 -5.06 21150.0 /
PLOG / 10.0 9.30E+27 -5.55 22900.0 /
PLOG / 100.0 3.80E+36 -7.58 31300.0 /
CH3CCH2 = CH3CHCH 1.60E+44 -12.16 52200.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 8.0E+43 -12.16 52200.0 / ! EST 0.1 atm /2
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PLOG / 0.1 1.60E+44 -12.16 52200.0 /
PLOG / 1.0 1.50E+48 -12.71 53900.0 /
PLOG / 10.0 5.10E+52 -13.37 57200.0 /
PLOG / 100.0 5.80E+51 -12.43 59200.0 /
aC3H5 = CH3CHCH 1.30E+55 -14.53 73800.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 6.50E+54 -14.53 73800.0 / ! EST 0.1 atm /2
PLOG / 0.1 1.30E+55 -14.53 73800.0 /
PLOG / 1.0 5.00E+51 -13.02 73300.0 /
PLOG / 10.0 9.70E+48 -11.73 73700.0 /
PLOG / 100.0 4.86E+44 -9.84 73400.0 /
aC3H5 = CH3CCH2 3.90E+59 -15.42 75400.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 1.45E+59 -15.42 75400.0 / ! EST 0.1 atm /2
PLOG / 0.1 3.90E+59 -15.42 75400.0 /
PLOG / 1.0 7.06E+56 -14.08 75868.0 /
PLOG / 2.0 4.80E+55 -13.59 75949.0 /
PLOG / 5.0 4.86E+53 -12.81 75883.0 /
PLOG / 10.0 6.40E+51 -12.12 75700.0 /
PLOG / 100.0 2.80E+43 -9.27 74000.0 /
C2H2+CH3=aC3H5 8.2E+53 -13.32 33200. ! 1999 Davis et al. RRKM
PLOG /0.039 4.1E+53 -13.32 33200. / ! EST 0.1 atm /2
PLOG /0.1 8.2E+53 -13.32 33200. /
PLOG /1.0 2.7E+53 -12.82 35700. /
PLOG /10.0 4.4E+49 -11.40 36700. /
PLOG /100.0 3.8E+44 -9.63 37600. /
pC3H4+H=aC3H5 1.1E+60 -14.56 28100. ! 1999 Davis et al. RRKM
PLOG /0.039 5.5E+59 -14.56 28100. / ! EST 0.1 atm /2
PLOG /0.1 1.1E+60 -14.56 28100. /
PLOG /1.0 4.9E+60 -14.37 31600. /
PLOG /10.0 2.2E+59 -13.61 34900. /
PLOG /100.0 1.6E+55 -12.07 37500. /
aC3H4+H=aC3H5 9.60E+61 -14.67 26000.0 ! 1999 Davis et al. RRKM
PLOG / 0.039 4.80E+61 -14.67 26000.0 / ! EST 0.1 atm /2
PLOG / 0.1 9.60E+61 -14.67 26000.0 /
PLOG / 1.0 1.52E+59 -13.54 26949.0 /
PLOG / 2.0 3.78E+57 -12.98 26785.0 /
PLOG / 5.0 7.34E+54 -12.09 26187.0 /
PLOG / 10.0 2.40E+52 -11.30 25400.0 /
PLOG / 100.0 6.90E+41 -8.06 21300.0 /
aC3H5+aC3H5 = pC3H4+C3H6 8.43E+10 0.0 -263 !2009 Kifer et al
! C3H6 reactions
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aC3H5+H(+M) = C3H6(+M) 2.00E+14 0.00 00.0 ! 1991 TSA

LOW / 1.33E+60 -12.00 5967.8 /

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C2H3+CH3 (+M) = C3H6(+M) 2.50E+13 0.000 00.00 ! 1986 TSA/HAM

LOW / 4.270E+58 -11.940 9769.80 /

TROE / 0.175 1340.6 60000.0 10139.8 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/C2H2/3.00/ C2H4/3.00/

C3H6 = H2 + pC3H4 1.18E+95 -23.6 125649 ! 2009 Kiefer et al.

C3H6 = H2 + aC3H4 1.18E+95 -23.6 125649 ! ref:C3H6 = H2 + pC3H4

! C3H6+H = C2H4+CH3 8.80E+16 -1.05 6461.0 ! 1991 TSA

C3H6+H = aC3H5+H2 1.73E+05 2.50 2490.0 ! 1991 TSA

! C3H6+H = CH3CCH2+H2 4.00E+05 2.50 9790.0 ! 1991 TSA

! C3H6+H = CH3CHCH+H2 8.04E+05 2.50 12283.0 ! 1991 TSA

C3H6+CH3 = aC3H5+CH4 2.20E+00 3.50 5675.0 ! 1991 TSA !

C3H6+CH3 = CH3CCH2+CH4 8.40E-01 3.50 11660.0 ! 1991 TSA !

C3H6+CH3 = CH3CHCH+CH4 1.35E+00 3.50 11848.0 ! 1991 TSA !

C3H6+C2H3 = C4H6+CH3 7.23E+11 1.35 5000.0 ! 1991 TSA !n value change in this work

C3H6+H = CH3CCH2+H2 1.49E+04 3.381 8909.5 !J.A. Miller and S.J. Klippenstein 2013 !

C3H6+H = CH3CHCH+H2 5.10E+02 3.234 12357 !J.A. Miller and S.J. Klippenstein 2013 !

DUPLICATE

C3H6+H = CH3CHCH+H2 3.97E+02 3.252 12007 !J.A. Miller and S.J. Klippenstein 2013 !

DUPLICATE

C3H6+H = C2H4+CH3 1.54E+09 1.3549 2542 !J.A. Miller and S.J. Klippenstein 2013

! PLOG/ 0.0013 1.54E+09 1.3549 2542/

! PLOG/ 0.0395 7.88E+10 0.87 3599.6/

! PLOG/ 1.000 2.67E+12 0.4736 5431.1/

! PLOG/ 10.00 9.25E+22 -2.5495 12898/

! PLOG/ 10.00 1.24E+05 2.5154 3679.1/

! PLOG/ 100.0 1.32E+23 -2.4248 16500/

! PLOG/ 100.0 2.51E+03 2.9088 3980.9/

! reactions of nC3H7

nC3H7+H(+M) = C3H8(+M) 3.60E+13 0.00 0.0 ! 1988 TSA

LOW / 3.01E+48 -9.32 5833.6/

TROE / 0.498 1314.0 1314.0 50000.0 /

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H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C3H6+H(+M) = nC3H7(+M) 1.33E+13 0.00 3260.7 ! 1991 TSA
LOW / 6.26E+38 -6.66 7000.0/
TROE / 1.000 1000.0 1310.0 48097.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
CH3+C2H4(+M)= nC3H7(+M) 2.55E+06 1.600 5700. ! 1988 TSA
LOW / 3.00E+63 -14.6 18170./
TROE /0.1894 277. 8748. 7891./
H2/2.00/ CH4/2.00/ C2H6/3.00/ AR/0.70/
nC3H7+H = C2H5+CH3 3.40E+18 -1.33 5386.0 ! 1988 TSA
nC3H7+H = C3H6+H2 1.80E+12 0.00 0.0 ! 1988 TSA
nC3H7+CH3 = CH4+C3H6 1.10E+13 -0.32 0.0 ! 1988 TSA
! reactions of iC3H7
iC3H7+H(+M) = C3H8(+M) 2.40E+13 0.00 0.0 ! 1988 TSA
LOW / 1.70E+58 -12.08 11263.7/
TROE / 0.649 1213.1 1213.1 13369.7 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C3H6+H(+M) = iC3H7(+M) 1.33E+13 0.00 1559.8 ! 1991 TSA
LOW / 8.70E+42 -7.50 4721.8/
TROE / 1.000 1000.0 645.4 6844.3/
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
iC3H7+H = CH3+C2H5 5.90E+23 -2.81 10009.0 ! 1988 TSA RRKM 0.1 atm
iC3H7+H = C3H6+H2 3.20E+12 0.00 0.0 ! 1988 TSA
iC3H7+CH3 = CH4 + C3H6 9.4E+10 0.68 0.0 ! 1988 TSA
! reactions of C3H8
C3H8+H = H2+nC3H7 1.30E+06 2.54 6756.0 ! 1988 TSA
C3H8+H = H2+iC3H7 1.30E+06 2.40 4471.0 ! 1988 TSA
C3H8+CH3 = CH4+nC3H7 9.03E-01 3.65 7153.0 ! 1988 TSA
C3H8+CH3 = CH4+iC3H7 1.51E+00 3.46 5480.0 ! 1988 TSA
!!!C4
! reactions of C4H2
C2H2+C2H2 = C4H2+H2 1.50E+13 0.0 42700 ! 2007 Gueniche et al.
C2H2+C2H = C4H2+H 9.60E+13 0.00 0.00 ! 1991 SHI/MIC, 1992 Koshi et al., 1993 Fahrat et al.
! reactions of nC4H3
C2H2+C2H(+M) = nC4H3(+M) 8.30E+10 0.899 -363.00 ! 1992 Wang
LOW / 1.240E+31 -4.718 1871.00/
TROE / 1.0 100. 5613. 13387./
H2/2.0/ CH4/2.0/ C2H6/3.0/ C2H2/2.5/ C2H4/2.5/
nC4H3 + H = C4H4 1.10E+42 -9.65 7000.0 ! 1997 Wang&Frenklach
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PLOG / 0.026 1.10E+42 -9.65 7000.0/
PLOG / 0.118 1.10E+42 -9.65 7000.0/
PLOG / 1.0 2.00E+47 -10.26 13070.0/
C4H2 + H = nC4H3 1.70E+49 -11.67 12804.0 ! 1997 Wang&Frenklach
PLOG / 0.026 1.70E+49 -11.67 12804.0/
PLOG / 0.118 3.30E+50 -11.80 15010.0/
PLOG / 1.0 1.10E+42 -8.72 15300.0/
nC4H3 = iC4H3 3.70E+61 -15.81 54890.0 ! 1997 Wang&Frenklach
PLOG / 0.026 3.70E+61 -15.81 54890.0/
PLOG / 0.118 1.00E+51 -12.45 51000.0/
PLOG / 1.0 4.10E+43 -9.49 53000.0/
C3H3+CH = nC4H3+H 5.00E+13 0.0 0.0 ! USC Mech V2.0 Estimated
C3H2+CH2 = nC4H3+H 5.00E+13 0.0 0.0 ! 1992 Miller&Melius
nC4H3+H = C4H2+H2 3.00E+13 0.00 0.0 ! = 0.5*C2H3+H USC Mech V2.0
nC4H3 + H = C2H2 + H2CC 1.60E+19 -1.60 2220.0 ! 1997 Wang&Frenklach 0.026 atm RRKM
nC4H3 + H = iC4H3 + H 2.40E+11 0.79 2410.0 ! 1997 Wang&Frenklach 0.026 atm RRKM
! reactions of iC4H3
C2H2+C2H(+M) = iC4H3(+M) 8.30E+10 0.899 -363.00 ! 1992 Wang
LOW / 1.240E+31 -4.718 1871.00/
TROE / 1.0 100. 5613. 13387./
H2/2.0/ CH4/2.0/ C2H6/3.0/C2H2/2.5/ C2H4/2.5/
C4H2+H(+M)=iC4H3(+M) 4.31E+10 1.160 1751.91 ! 1992 Wang
LOW / 2.30e+45 -8.100 2507.17/
TROE / 0.0748 1.00 -4216.00/
H2/2.00/ AR/0.70/ CH4/2.00/ C2H6/3.00/
iC4H3 + H = C4H4 4.20E+44 -10.27 7890.0 ! 1997 Wang&Frenklach
PLOG / 0.026 4.20E+44 -10.27 7890.0 /
PLOG / 0.118 5.30E+46 -10.68 9270.0 /
PLOG / 1.0 3.40E+43 -9.01 12120.0/
iC4H3+H = C2H2+H2CC 2.40E+19 -1.60 2800.0 ! 1997 Wang&Frenklach 0.026 atm RRKM
iC4H3+H = C4H2+H2 6.00E+13 0.00 0.0 ! = C2H3+H USC Mech V2.0
C3H3+CH = iC4H3+H 5.00E+13 0.0 0.0 ! USC Mech V2.0 Estimated
! reactions of C4H4
H2CC+C2H2(+M) = C4H4(+M) 3.50E+05 2.055 -2400. ! 1999 Laskin&Wang
LOW / 1.40E+60 -12.599 7417./
TROE / 0.98 560. 580. 4164./
H2/2.0/ CH4/2.0/ C2H2/3.0/ C2H4/3.0/ C2H6/3.0/
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C2H3+C2H = C4H4 1.00E+14 0.00 0.0 ! 1988 Duran et al.

C3H3+CH2* = C4H4+H 4.00E+13 0.0 0.0 ! 2007 Gueniche et al.

C4H4+H = nC4H3+H2 6.65E+05 2.53 12240. ! 1997 Wang&Frenklach

C4H4+H = iC4H3+H2 3.33E+05 2.53 9240. ! 1997 Wang&Frenklach

C2H3+C2H2=C4H4+H 5.00E+14 -0.71 6700. ! 1997 Wang&Frenklach 0.026 atm RRKM

C3H3+CH2=C4H4+H 5.00E+13 0.00 0.0 ! 1992 Miller&Melius

C3H2+CH3=C4H4+H 5.00E+12 0.00 0.0 ! USC Mech V2.0

! reactions of nC4H5

C2H3 + C2H2 = nC4H5 1.10E+31 -7.14 5600. ! 1997 Wang&Frenklach

PLOG / 0.013 1.10E+31 -7.14 5600. /

PLOG / 0.026 1.10E+32 -7.33 6200. /

PLOG / 0.118 2.40E+31 -6.95 5600. /

PLOG / 1.0 9.30E+38 -8.76 12000./

PLOG / 10.0 8.10E+37 -8.09 13400./

C4H4 + H = nC4H5 1.20E+51 -12.57 12300. ! 1997 Wang&Frenklach

PLOG / 0.013 1.20E+51 -12.57 12300./

PLOG / 0.026 4.20E+50 -12.34 12500./

PLOG / 0.118 1.10E+50 -11.94 13400./

PLOG / 1.0 1.30E+51 -11.92 16500./

PLOG / 10.0 6.20E+45 -10.08 15800./

nC4H5 = iC4H5 2.40E+60 -16.08 47500. ! 1997 Wang&Frenklach

PLOG / 0.013 2.40E+60 -16.08 47500./

PLOG / 0.026 1.30E+62 -16.38 49600./

PLOG / 0.118 4.90E+66 -17.26 55400./

PLOG / 1.0 1.50E+67 -16.89 59100./

PLOG / 10.0 2.00E+60 -14.46 58600./

nC4H5+H = iC4H5+H 1.00E+36 -6.26 17486. ! 1997 Wang&Frenklach 0.026 atm RRKM

C2H3+C2H3 = nC4H5+H 1.10E+24 -3.28 12395. ! 1997 Wang&Frenklach 0.026 atm RRKM

nC4H5+H = C4H4+H2 1.50E+13 0.00 0.0 ! 1997 Wang&Frenklach

! reactions of iC4H5

C2H3 + C2H2 = iC4H5 5.00E+34 -8.42 7900. ! 1997 Wang&Frenklach

PLOG / 0.013 5.00E+34 -8.42 7900. /

PLOG / 0.026 2.10E+36 -8.78 9100. /

PLOG / 0.118 1.00E+37 -8.77 9800. /

PLOG / 1.0 1.60E+46 -10.98 18600./

PLOG / 10.0 5.10E+53 -12.64 28800./

C4H4 + H = iC4H5 6.10E+53 -13.19 14200. ! 1997 Wang&Frenklach

PLOG / 0.013 6.10E+53 -13.19 14200./

PLOG / 0.026 9.60E+52 -12.85 14300./

PLOG / 0.118 2.10E+52 -12.44 15500./

PLOG / 1.0 4.90E+51 -11.92 17700./

PLOG / 10.0 1.50E+48 -10.58 18800./

C2H3+C2H3 = iC4H5+H 1.50E+30 -4.95 12958. ! 1997 Wang&Frenklach 0.026 atm RRKM

iC4H5+H = C4H4+H2 3.0E+13 0.00 0. ! 1997 Wang&Frenklach

iC4H5+H=C3H3+CH3 1.0E14 0.00 0. ! 2009 Hansen et al C3H4 FLAME

! reactions of C4H5-2

C4H5-2 = iC4H5 1.30E+62 -16.38 49600. ! nC4H5=¿iC4H5 1997 Wang&Frenklach 0.026 atm RRKM

iC4H5+H = C4H5-2+H 1.00E+36 -6.26 17486. ! = nC4H5+H=¿iC4H5+H 0.026 atm RRKM 1997 Wang&Frenklach

! Ractions of c-C4H5

c-C4H5 + H = C4H6 1.000E+13 0.000 0.00 ! Est. HW, fast c-C4H6 -¿ C4H6 - Lifshitz USC Mech V2.0

c-C4H5 + H = C2H4 + C2H2 1.000E+13 0.000 0.00 ! Est. HW USC Mech V2.0

c-C4H5 = C4H4 + H 3.000E+12 0.000 52000.00 ! Est. HW USC Mech V2.0

c-C4H5 = C2H3 + C2H2 2.000E+12 0.000 58000.00 ! Est. HW USC Mech V2.0

! reactions of C4H6

C4H6 = C4H4+H2 8.33E+13 0.0 94700. !

PLOG / 0.039 8.33E+13 0.0 94700./ ! EST 2.5E+15 /30

PLOG / 1.0 2.50E+15 0.0 94700./ ! 1996 Hidaka et al.

C4H6 = H2CC+C2H4 1.00E+13 0.0 85000.0 ! EST

C2H3 + C2H3 = C4H6 7.00E+57 -13.82 17629. ! 1997 Wang&Frenklach

PLOG / 0.026 7.00E+57 -13.82 17629./

PLOG / 0.118 1.50E+52 -11.97 16056./

PLOG / 1.0 1.50E+42 -8.84 12483./

C4H6 = iC4H5 + H 8.20E+51 -10.92 118409. ! 1997 Wang&Frenklach

PLOG / 0.026 8.20E+51 -10.92 118409./

PLOG / 0.118 3.30E+45 -8.95 115934./

PLOG / 1.0 5.70E+36 -6.27 112353./

C4H6 = nC4H5 + H 3.50E+61 -13.87 129677. ! 1997 Wang&Frenklach

PLOG / 0.026 3.50E+61 -13.87 129677./

PLOG / 0.118 8.50E+54 -11.78 127472./

PLOG / 1.0 5.30E+44 -8.62 123608./

C4H6+H = nC4H5+H2 1.33E+06 2.53 12240. ! =C2H4+H USC Mech V2.0

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C4H6+H = iC4H5+H2 6.65E+05 2.53 9240. ! USC Mech V2.0 Estimated
C4H6+H = C2H4+C2H3 1.46E+30 -4.34 21647. ! USC Mech II (1997 Wang&Frenklach 1 atm)
C4H6+H = pC3H4+CH3 2.00E+12 0.0 7000. ! USC Mech V2.0 Estimated
C4H6+H = aC3H4+CH3 2.00E+12 0.0 7000. ! USC Mech V2.0 Estimated
C4H6+CH3 = nC4H5+CH4 2.00E+14 0.0 22800. ! 1996 Hidaka et al.
C4H6+CH3 = iC4H5+CH4 1.00E+14 0.0 19800. ! 1996 Hidaka et al.
C4H6+C2H3 = nC4H5+C2H4 5.00E+13 0.0 22800. ! 1996 Hidaka et al.
C4H6+C2H3 = iC4H5+C2H4 2.50E+13 0.0 19800. ! 1996 Hidaka et al.
C4H6+C3H3 = nC4H5+aC3H4 1.00E+13 0.0 22500. ! 1996 Hidaka et al.
C4H6+C3H3 = iC4H5+aC3H4 0.50E+13 0.0 19500. ! 1996 Hidaka et al.
C4H6+aC3H5 = nC4H5+C3H6 1.00E+13 0.0 22500. ! USC Mech V2.0 Estimated
C4H6+aC3H5 = iC4H5+C3H6 0.50E+13 0.0 19500. ! USC Mech V2.0 Estimated
! reactions of 1,2-C4H6
C4H612 = C4H6 1.00E+12 0.0 65000 !
PLOG / 0.039 1.00E+12 0.0 65000/ ! EST 3.00E+13 /30
PLOG / 1.0 3.00E+13 0.0 65000/ ! 1996 Hidaka et al
C3H3+CH3 (+M) = C4H612 (+M) 1.50E+12 0.0 0.0 ! 1997 Wang&Frenklach
LOW / 2.60E+57 -11.94 9770.0/
TROE / 0.175 1340.6 60000.0 9769.8 /
H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/
C4H612+H = nC4H5+H2 1.33E+06 2.53 12240. ! = C2H4+H
C4H612 = iC4H5+H 2.10E+14 0.0 92600. !
PLOG / 0.039 2.10E+14 0.0 92600./ ! EST 4.20E+15 /20
PLOG / 1.0 4.20E+15 0.0 92600./ ! 1995 Leung et al.
C4H612+H = C4H6+H 2.00E+13 0.0 4000. ! USC Mech V2.0 Estimated
C4H612+H = iC4H5+H2 1.70E+05 2.5 2490. ! = C3H6+H USC Mech V2.0
C4H612+H = aC3H4+CH3 2.00E+13 0.0 2000. ! 1997 Wang&Frenklach
C4H612+H = pC3H4+CH3 2.00E+13 0.0 2000. ! 1997 Wang&Frenklach
C4H612+CH3 = iC4H5+CH4 7.00E+13 0.0 18500. ! 1988 Kern et al.
! reactions of C4H6-2
C4H6-2 = C4H6 1.00E+12 0.000 65000. !
PLOG / 0.039 1.00E+12 0.000 65000./ ! EST 3.00E+13 /30
PLOG / 1.0 3.00E+13 0.000 65000./ ! 1996 Hidaka et al.
C4H6-2 = C4H612 1.00E+12 0.000 67000. !
PLOG / 0.039 1.00E+12 0.000 67000./ ! EST 3.00E+13 /30
PLOG / 1.0 3.00E+13 0.000 67000./ ! 1996 Hidaka et al.
C4H6-2+H = C4H612+H 2.00E+13 0.0 4000. ! USC Mech V2.0 Estimated
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C4H6-2+H = C4H5-2+H2 3.40E+05 2.5 2490. ! = C3H6+H USC Mech V2.0
C4H6-2+H = CH3+pC3H4 2.60E+5 2.500 1000. ! 1996 Hidaka et al.
C4H6-2 = H+C4H5-2 1.67E+14 0.000 87300. !
PLOG / 0.039 1.67E+14 0.000 87300./ ! EST 5.00E+15 /30
PLOG / 1.0 5.00E+15 0.000 87300./ ! 1996 Hidaka et al.
C4H6-2+CH3 = C4H5-2+CH4 1.40E+14 0.0 18500. ! USC Mech V2.0 Estimated
! reactions of saxC4H7
SAXC4H7(+M) = C4H6+H(+M) 4.70E+08 1.32 44697.6 ! JetSurF 2.0
LOW / 4.6E-37 15.37 -603.1/
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
SAXC4H7+H = C4H612+H2 1.80E+13 0.0 0.0 ! EST JetSurF 2.0
C4H612+H = SAXC4H7 1.20E+10 0.69 3000 ! 2007 Gueniche et al./10
SAXC4H7+H = C4H6+H2 1.80E+13 0.00 0.0 ! (aC3H5+H) JetSurF 2.0
SAXC4H7+CH3=C4H6+CH4 3.00E+12 -0.32 -131.0 ! aC3H5+CH3 = aC3H4+CH4 JetSurF 2.0
SAXC4H7+CH3 = C4H612+CH4 1.00E+13 0.00 0.0 ! EST JetSurF 2.0
SAXC4H7+C2H3 = C4H6+C2H4 1.00E+13 0.00 0.0 ! EST JetSurF 2.0
SAXC4H7+C2H3 = C4H612+C2H4 1.00E+13 0.00 0.0 ! EST JetSurF 2.0
! reactions of C4H7
C4H7 = C4H6+H 1.27E+24 -4.75 23777 !
PLOG / 0.033 1.27E+24 -4.75 23777 / ! 2009 Kiefer et al.
PLOG / 0.066 1.38E+26 -5.221 25729 / ! 2009 Kiefer et al.
PLOG / 0.132 1.75E+28 -5.709 27764 / ! 2009 Kiefer et al.
PLOG / 0.197 3.16E+29 -6.003 28985 / ! 2009 Kiefer et al.
PLOG / 0.263 2.69E+30 -6.222 29890 / ! 2009 Kiefer et al.
PLOG / 1.0 2.48E+53 -12.30 52000 / ! 1997 Wang&Frenklach
PLOG / 10 1.85E+48 -10.50 51770 / ! 1997 Wang&Frenklach
C2H4+C2H3 = C4H7 1.23E+35 -7.76 9930.0 ! 1997 Wang&Frenklach
PLOG / 0.039 6.15E+34 -7.76 9930.0 / ! EST 0.1 atm/2
PLOG / 0.1 1.23E+35 -7.76 9930.0 /
PLOG / 1.0 7.93E+38 -8.47 14220.0/
PLOG / 10 2.99E+36 -7.40 15480.0/
C4H7+H = SAXC4H7+H 1.00E+13 0.00 0.0 ! EST JetSurF 2.0
C4H7+H = CH3+aC3H5 2.00E+21 -2.00 11000.0 ! Estimated USC Mech V2.0
C4H7+H = C4H6+H2 1.80E+12 0.00 0.0 ! = nC3H7+H USC Mech V2.0
C4H7+CH3 = C4H6+CH4 1.10E+13 0.00 0.0 ! = nC3H7+CH3 USC Mech V2.0
! reactions of C4H7-2 CH3CCHCH3

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C4H7-2 = SAXC4H7 2.00E+12 0.0 47000 ! 2007 Gueniche et al./10
C4H7-2 = CH3+aC3H4 2.00E+12 0.0 32500 ! 2007 Gueniche et al./10
C4H7-2 = C4H7 3.30E+08 1.0 43300 ! 2007 Gueniche et al./10
C4H612+H = C4H7-2 1.30E+12 0.0 3200 ! 2007 Gueniche et al./10
CH3CCHCH3=pC3H4+CH3 2.00E+12 0.0 31500 ! 2007 Gueniche et al./10
C4H7-2+H=pC3H4+CH4 3.00E+13 0.0 0.0 ! EST
! reactions of iC4H7 iC4H7-1
iC4H7=aC3H4+CH3 1.00E+12 0.0 51000 ! 2009 Yasunaga et al. /10
iC4H7+H=aC3H4+CH4 6.31E+13 0.0 0.0 ! 2009 Yasunaga et al.
iC4H7=SAXC4H7 6.00E+13 0. 70000 ! 2012 Zhang et al.
iC4H7+H=SAXC4H7+H 1.47E+13 0.26 4103 ! Ref aC3H4+H=pC3H4+H
iC4H7+H = aC3H5+CH3 2.20E+51 -9.98 37730.0 ! =(aC3H5+H) TS5 0.1 atm USC Mech V2.0
iC4H7+H = CH3CCH2+CH3 2.20E+51 -9.98 37730.0 ! =(aC3H5+H) TS5 0.1 atm USC Mech V2.0
iC4H7-1=pC3H4+CH3 1.30E+14 0.0 37000 ! 2009 Yasunaga et al.
iC4H7-1=iC4H7 5.00E+12 0.0 36000 ! 2009 Yasunaga et al.
! reactions of C4H8-1
aC3H5+CH3(+M)=C4H8-1(+M) 1.00E+11 -0.32 -262. ! 1991 TSA !A value change in this work change
LOW /3.51E+60 -12.97 6000./
TROE / 0.896 60000 1606 6118/
H2/2.0/ CH4/2.0/ C2H6/3.0/
AR/0.7/
C2H5+C2H3(+M) = C4H8-1(+M) 1.50E+13 0.00 0.0 ! 1986 TSA/HAM
LOW / 1.55E+56 -11.79 8984.5/
TROE / 0.198 2277.9 60000.0 5723.2 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C4H7+H(+M) = C4H8-1(+M) 3.60E+13 0.00 0.0 ! = nC3H7+H USC Mech V2.0
LOW / 3.01E+48 -9.32 5833.6/
TROE / 0.498 1314.0 1314.0 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
SAXC4H7+H(+M) = C4H8-1(+M) 2.00E+14 0.00 0.0 ! (ac3H5+H) JetSurF 2.0
LOW / 2.66E+60 -12.00 5967.8 / ! 2*(aC3H5+H)
H2/2/ CH4/2/ C2H6/3/
C4H8-1+H=C4H8-2+H 5.00E+14 -0.26 7600.0 ! Ref: pC3H4+H = aC3H4+H in USC Mech V2.0
C4H7-2+H = C4H8-1 1.00E+13 0.0 0.0 ! EST 2012 Zhang et al.
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C4H8-1+H = SAXC4H7+H2 1.30E+06 2.40 4471.0 ! (C3H8+H) USC Mech V2.0

C4H8-1+H = C4H7+H2 6.50E+05 2.5 6756 ! Ref C6H12-1E+H=P1XC6H11-1E+H2 in 2009 Kiefer et al.

C4H8-1+H = C4H7-2+H2 4.00E+05 2.50 9790.0 ! Ref to C3H6+H = CH3CCH2+H2

C4H8-1+H = C3H6+CH3 3.20E+22 -2.39 11180 ! 2012 Zhang et al.

C4H8-1+H = C2H4+C2H5 8.80E+16 -1.05 6461.0 ! Ref C3H6+H = C2H4+CH3

C4H8-1+CH3 = SAXC4H7+CH4 2.82E+00 3.60 7153 ! Ref C6H12-1E+CH3=S3XC6H11-1E+CH4 in 2009 Kiefer et al.

C4H8-1+CH3 = C4H7+CH4 4.50E-01 3.65 7153.0 ! (C3H8+CH3) USC Mech V2.0

! reactions of C4H8-2

CH3CHCH+CH3(+M) = C4H8-2(+M) 5.00E+13 0.0 0.00 ! Ref to C2H3+CH3(+M)=C3H6(+M)

LOW / 8.54E+58 -11.940 9769.80/

TROE / 0.175 1340.6 60000.0 10139.8/

H2/2/ CH4/2/ C2H6/3/ AR/0.7/C2H2/3.00/ C2H4/3.00/

SAXC4H7+H(+M) = C4H8-2(+M) 2.00E+14 0.00 0.0 ! (ac3H5+H) JetSurF 2.0

LOW / 2.66E+60 -12.00 5967.8 / ! 2*(aC3H5+H)

H2/2/ CH4/2/ C2H6/3/

C4H8-2 = aC3H5+CH3 7.5E+65 -15.6 97300 ! 2012 Zhang et al.

C4H8-2+H = SAXC4H7+H2 3.16E+06 2.5 6756 ! 2012 Zhang et al.

C4H8-2+H=CH3CCHCH3+H2 1.32E+06 2.53 12240.0 ! EST

C4H8-2+H = C3H6+CH3 3.46E+17 -1.05 6461.0 ! 2012 Zhang et al.

C4H8-2+CH3 = SAXC4H7+CH4 4.40E+00 3.50 5675.0 ! Ref C3H6+CH3=aC3H5+CH3 x2 in USC Mech V2.0

C4H8-2+H = C4H7+H2 3.46E+05 2.50 2490.0 ! Ref (C3H6+H)*2 TS5 k(a) in USC Mech V2.0

C4H8-2+CH3 = C4H7+CH4 4.40E+00 3.50 5675.0 ! Ref (C3H6+CH3)*2 TS5 k(c) in USC Mech V2.0

! reactions of iC4H8

iC4H7+H(+M) = iC4H8(+M) 2.00E+11 0.00 0.0 !(=(aC3H5+H) TS5 600cm-1) USC Mech V2.0 !A value change in this work change

LOW / 1.33E+60 -12.00 5967.8 /

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/

AR/0.7/

CH3CCH2+CH3(+M) = iC4H8(+M) 2.50E+10 0.00 0.0 ! Ref to C2H3+CH3 (+M) = C3H6(+M) ! !A value change in this work change

LOW / 4.270E+58 -11.940 9769.80/

```
TROE / 0.175 1340.6 60000.0 10139.8 /
H2/2/ CH4/2/ C2H6/3/
AR/0.7/
iC4H8+H = iC4H7+H2 1.72E+14 0.0 8000 ! 2009 Yasunaga et al. !
iC4H8+H = iC4H7-1+H2 1.20E+14 0.0 13000 ! 2009 Yasunaga et al. !
! iC4H8+H = C3H6+CH3 8.80E+16 -1.05 6461.0 ! Ref C3H6+H = C2H4+CH3 (91TSA RRKM 0.1 atm) in USC Mech V2.0
iC4H8+CH3 = iC4H7+CH4 4.40E+00 3.50 5675.0 ! Ref C3H6+CH3=aC3H5+CH3 x2 in USC Mech V2.0
iC4H8+CH3 = iC4H7-1+CH4 2.00E+12 0.0 15000 ! 2009 Yasunaga et al.
iC4H8+H = C3H6+CH3 8.80E+16 -1.05 6461.0 !Ref USC Mech II
PLOG/ 0.1 8.80E+16 -1.05 6461.0 / !Ref USC Mech II
PLOG/ 1.0 8.00E+21 -2.39 11180.0 / !Ref USC Mech II
PLOG/ 10 3.30E+24 -3.04 15610.0 / !Ref USC Mech II
! reactions of pC4H9
pC4H9(+M) = C2H4+C2H5(+M) 1.00E+13 0.00 28366.4 ! EST
LOW / 7.10E-35 15.41 -600.0 /
TROE / -5.91 333.0 28.0 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C4H8-1+H(+M) = pC4H9(+M) 1.33E+13 0.00 3260.7 ! =(C3H6+H) TS5 600 cm-1 USC Mech V2.0
LOW / 6.26E+38 -6.66 7000.0 /
TROE / 1.000 1000.0 1310.0 48097.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
pC4H9+H = C2H5+C2H5 3.40E+18 -1.33 5386.0 ! =(nC3H7+H) TS3 0.1 atm USC Mech V2.0
pC4H9+CH3 = C4H8-1+CH4 1.10E+13 0.00 0.0 ! =(nC3H7+CH3) TS3 USC Mech V2.0
! reactions of sC4H9
C3H6+CH3(+M) = sC4H9(+M) 1.70E+11 0.00 7403.6 ! TS5 600cm-1 USC Mech V2.0
LOW / 2.31E+28 -4.27 1831.0 /
TROE / 0.565 60000.0 534.2 3007.2 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C4H8-1+H(+M) = sC4H9(+M) 1.33E+13 0.00 1559.8 ! =(C3H6+H) TS5 600 cm-1 USC Mech V2.0
LOW / 8.70E+42 -7.50 4721.8 /
TROE / 1.000 1000.0 645.4 6844.3 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
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C4H8-2+H(+M) = sC4H9(+M) 1.33E+13 0.00 1559.8 ! =(C3H6+H=iC3H7) TS5 600cm-1 USC Mech V2.0
LOW / 8.70E+42 -7.50 4721.8 /
TROE / 1.000 1000.0 645.4 6844.3 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
sC4H9+H = C4H8-1+H2 3.20E+12 0.00 0.0 ! =(iC3H7+H) TS3 USC Mech V2.0
sC4H9+H = C4H8-2+H2 2.10E+12 0.00 0.0 ! =(iC3H7+H)*2/3 TS3 USC Mech V2.0
sC4H9+CH3 = CH4+C4H8-1 2.20E+14 -0.68 0.0 ! =(iC3H7+CH3) TS3 USC Mech V2.0
sC4H9+CH3 = CH4+C4H8-2 1.50E+14 -0.68 0.0 ! =(iC3H7+CH3)*2/3 TS3 USC Mech V2.0
! reactions of iC4H9
C3H6+CH3(+M) = iC4H9(+M) 9.60E+10 0.00 8003.6 ! TS5 600cm-1 USC Mech V2.0
LOW / 1.30E+28 -4.27 2431.1 /
TROE / 0.565 60000.0 534.2 3007.2 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
iC4H8+H(+M) = iC4H9(+M) 1.33E+13 0.00 3260.7 ! =(C3H6+H=nC3H7) TS5 600 cm-1 USC Mech V2.0
LOW / 6.26E+38 -6.66 7000.0 /
TROE / 1.000 1000 1310.0 48097.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
iC4H9+H = iC3H7+CH3 1.10E+32 -5.04 16760.0 ! TS4 eq 0.1 atm USC Mech V2.0
iC4H9+H = iC4H8+H2 9.00E+11 0.00 0.0 ! TS4 USC Mech V2.0
iC4H9+CH3 = iC4H8+CH4 6.00E+12 -0.32 0.0 ! TS4 USC Mech V2.0
! reactions of tC4H9
tC4H9(+M) = iC4H8+H(+M) 8.30E+13 0.00 38150.4 ! TS4 600cm-1 USC Mech V2.0
LOW / 1.90E+41 -7.36 36631.7/
TROE / 0.293 649.0 60000 3425.9 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
tC4H9+H = iC3H7+CH3 2.80E+34 -5.69 20500.0 ! TS4 eq 0.1 atm USC Mech V2.0
tC4H9+H = iC4H8+H2 5.42E+12 0.00 0.0 ! TS4 USC Mech V2.0
tC4H9+CH3 = iC4H8+CH4 3.80E+15 -1.00 0.0 ! TS4 USC Mech V2.0
!!!C5
! reactions of C5H2 to C5H4
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C2H3+C3H3=C5H4+H2 1.00E+13 0.0 0.0 ! EST
C4H2+CH2*=C5H3+H 1.30E+13 0.0 0.0 ! MIT [1992 Miller&Melius]
C4H2+CH2=C5H3+H 3.00E+13 0.0 0.0 ! MIT [1992 Miller&Melius]
C4H2+CH=C5H2+H 1.00E+14 0.0 0.0 ! MIT [1992 Miller&Melius]
C5H3+H=C5H2+H2 6.03E+13 0.0 15103.0 ! MIT [CH3+H, 1992 Baulch et al.]
cC5H4=C5H4 1.00E+13 0.0 6000.0 ! MIT [2002 Richter&Howard, estimate]
C4H2+CH3=C5H4+H 2.40E+09 0.91 20700.0 ! Ref: C2H2+CH3=aC3H4+H 1999 Davis et al.
C4H+CH4=C5H4+H 2.40E+09 0.91 20700.0 ! Ref: C2H2+CH3=aC3H4+H 1999 Davis et al.
aC3H4+C2H=C5H4+H 9.60E+13 0.00 0.0 ! Ref: C2H2+C2H=C4H2+H
C5H3+H=C5H4 1.00E+14 0.0 0.0 ! 2000 Alzueta et al. est /2
C5H4+H=C5H3+H2 1.00E+13 0.0 0.0 ! EST
! reactions of C5H5
C2H3+C3H3=lC5H5+H 1.00E+13 0.0 0.0 ! EST
C3H3+C2H2=C5H5 6.17E+66 -15.7 47729 ! 2000 Moskaleva&Lin
PLOG/ 0.132 6.17E+66 -15.7 47729/ !
PLOG/ 1.000 6.87E+55 -12.5 42000/ !
PLOG/ 10.00 1.13E+43 -8.80 34983/ !
C5H5+H=cC5H4+H2 3.23E+07 2.095 15842.0 ! MIT [1997 Mebel et al. A1+H]
C5H5+CH3=cC5H4+CH4 2.00E+12 0.0 15060.0 ! MIT [1989 Zhang et al., A1+CH3]
lC5H5+H=C5H4+H2 1.81E+12 0.0 0.0 ! MIT [1986 TSA/HAM, C2H5+H]
lC5H5+CH3=C5H4+CH4 1.95E+13 -0.50 0.0 ! MIT [1986 TSA/HAM,C2H5+CH3]
C5H5=lC5H5 1.64E+96 -23.50 137409.0 ! MIT [2000 Moskaleva&Lin, 100 torr]
! reactions of C5H6
C5H5 + H (+M)= C5H6 (+M) 1.000E+14 0.000 0.00 ! JetSurF 2.0
LOW / 4.400E+80 -18.280 12994.0/
TROE / 0.068 400.7 4135.8 5501.9 /
H2/2.0/ CH4/2.0/
C4H5-2+C2H4=C5H6+CH3 5.00E+14 0.0 25000.0 ! USC Mech V2.0
C5H6+H=C2H2+aC3H5 7.740E+36 -6.180 32890.00 ! 1998 Zhong&Bozzelli
C5H6+H=lC5H7 8.27E+125 -32.30 82348.00 ! 2002 Moskaleva&Lin 8.270E+126 /10
C5H6+H=C5H5+H2 3.030E+08 1.710 5590.00 ! 2002 Moskaleva&Lin
C5H6+CH3=C5H5+CH4 5.00E+11 0.0 5000.0 ! 2001 Mac&Bac
C5H6+C2H3=C5H5+C2H4 1.20E-1 4.0 0.0 ! 1998 Zhong&Bozzelli
! reactions of C5H7
aC3H5+C2H2=lC5H7 4.1E+29 -6.2 12824.0
```

PLOG / 0.039 4.1E+29 -6.2 12824./ ! EST 1.0 atm /20

PLOG / 1.0 8.38E+30 -6.2 12824./ ! USC Mech V2.0

aC3H5+C2H3=lC5H7+H 5.00E+12 0.0 0.0 ! USC Mech V2.0 (est) /2

iC4H5+CH3=lC5H7+H 1.00E+13 0.0 0.0 ! Est

aC3H4+C2H3 = P1XCH2C4H5-13E 1.23E+35 -7.76 9930.0 ! Ref to C2H4+C2H3 = C4H7

PLOG / 0.039 6.15E+34 -7.76 9930.0 /

PLOG / 0.1 1.23E+35 -7.76 9930.0 /

PLOG / 1.0 7.93E+38 -8.47 14220.0/

PLOG / 10 2.99E+36 -7.40 15480.0/

C2H2 + CH3CCH2 = S4XC4H4-13E2M 1.10E+31 -7.14 5600. ! Ref to C2H3 + C2H2 = nC4H5

PLOG / 0.013 1.10E+31 -7.14 5600. /

PLOG / 0.026 1.10E+32 -7.33 6200. /

PLOG / 0.118 2.40E+31 -6.95 5600. /

PLOG / 1.0 9.30E+38 -8.76 12000./

PLOG / 10.0 8.10E+37 -8.09 13400./

C2H3 + pC3H4 = T4XC5H7-13E 1.10E+31 -7.14 5600. ! Ref to C2H3 + C2H2 = nC4H5

PLOG / 0.013 1.10E+31 -7.14 5600. /

PLOG / 0.026 1.10E+32 -7.33 6200. /

PLOG / 0.118 2.40E+31 -6.95 5600. /

PLOG / 1.0 9.30E+38 -8.76 12000./

PLOG / 10.0 8.10E+37 -8.09 13400./

C4H4+CH3 = S1XC4H4-13E2M 1.40E+32 -7.14 10000.0 ! Ref to C2H2+CH3 = CH3CHCH

PLOG / 0.039 7.0E+31 -7.14 10000.0 /

PLOG / 0.1 1.40E+32 -7.14 10000.0 /

PLOG / 1.0 3.20E+35 -7.76 13300.0 /

PLOG / 10.0 2.40E+38 -8.21 17100.0 /

PLOG / 100.0 1.40E+39 -8.06 20200.0 /

C2H2 + CH3CHCH = S1XC5H7-13E 1.10E+31 -7.14 5600. ! Ref to C2H3 + C2H2 = nC4H5

PLOG / 0.013 1.10E+31 -7.14 5600. /

PLOG / 0.026 1.10E+32 -7.33 6200. /

PLOG / 0.118 2.40E+31 -6.95 5600. /

PLOG / 1.0 9.30E+38 -8.76 12000./

PLOG / 10.0 8.10E+37 -8.09 13400./

! reactions of C5H8

C5H8-13E+H = C2H4+CH3CHCH 1.46E+30 -4.34 21647.0 ! =(C4H6+H) JetSurF 2.0 !

C5H8-13E+H = C4H6-2+CH3 2.00E+12 0.0 7000. ! =(C4H6+H) JetSurF 2.0

C5H8-13E+H = C4H612+CH3 2.00E+12 0.0 7000. ! =(C4H6+H) JetSurF 2.0

C5H8-13E+H = lC5H7+H2 1.73E+05 3.25 2490.0 ! (=C3H6+H) JetSurF 2.0 !!n value change in this work

C5H8-13E+CH3 = lC5H7+CH4 2.20E+00 3.50 5675.0 ! =(C3H6+CH3) JetSurF 2.0 !

C5H8-12E = C5H8-13E 1.1E+13 0.00 67000.0 !

PLOG / 0.039 1.1E+13 0.00 67000.0 / ! /20 EST

PLOG / 1.0 2.20E+14 0.00 67000.0/ ! JetSurF 2.0

C5H8-13E = C5H8-14E 1.1E+13 0.00 67000.0 ! similar C5H8-12E = C5H8-13E

PLOG / 0.039 1.1E+13 0.00 67000.0 / ! /20 EST

PLOG / 1.0 2.20E+14 0.00 67000.0/ ! JetSurF 2.0

C5H8-12E = C2H4+pC3H4 3.30E+11 0.00 58100.0 !

PLOG / 0.039 3.30E+11 0.00 58100.0 / ! /20 EST

PLOG / 1.0 6.60E+12 0.00 58100.0/ ! JetSurF 2.0

nC4H5+CH3 = C5H8-13E 3.60E+12 0.00 0.0 !

! PLOG / 0.039 3.60E+12 0.00 0.0 / ! /20 EST

! PLOG / 1.0 7.23E+13 0.00 0.0/ ! 04/LAU-FAR JetSurF 2.0

C5H8-14E+H = aC3H5+C2H4 1.60E+22 -2.39 11180.0 ! = C3H6+H JetSurF 2.0

C5H8-14E+H = lC5H7+H2 1.15E+05 2.50 2490.0 ! (=C3H6+H) JetSurF 2.0

C5H8-14E+H = C4H6+CH3 2.00E+12 0.0 7000. ! =(C4H6+H) JetSurF 2.0

C5H8-14E+CH3 = lC5H7+CH4 1.47E+00 3.50 5675.0 ! =(C3H6+CH3) JetSurF 2.0

C4H5-13E2M+H = C3H6+C2H3 1.46E+30 -4.34 21647.0 ! =(C4H6+H) JetSurF 2.0

C4H5-13E2M+H = CH3CCH2+C2H4 1.46E+30 -4.34 21647.0 ! =(C4H6+H)

C4H5-13E2M+H = C4H6+CH3 8.00E+21 -2.39 11180.0 ! 1991 TSA RRKM 1 atm JetSurF 2.0

C4H5-13E2M+H = P1XCH2C4H5-13E+H2 1.20E+06 2.54 6760.0 ! 1989 TSA (=iC4H8+H) JetSurF 2.0

C4H5-13E2M+CH3 = P1XCH2C4H5-13E+CH4 2.20E+00 3.50 5675.0 ! =(C3H6+CH3) JetSurF 2.0

CH3+iC4H5 = C4H5-13E2M 1.00E+12 0.00 0.0 !

PLOG / 0.039 1.00E+12 0.00 0.0 / ! /20 EST

PLOG / 1.0 2.00E+13 0.0 0.0/ ! JetSurF 2.0

P1XCH2C4H5-13E+H(+M) = C4H5-13E2M(+M) 2.00E+14 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M)

LOW / 1.33E+60 -12.00 5967.8/

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

! reactions of C5H9

S3XC5H9-1E(+M) = C4H6+CH3(+M) 3.39E+11 0.66 32262.9 ! Ref S3XC6H11-1E(+M) = C4H6+C2H5(+M) in JetSurF 2.0

LOW / 4.00E-42 18.05 -602.6 /

TROE / -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S3XC5H9-1E(+M) = C5H8-13E+H(+M) 4.70E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M)

LOW / 4.6E-37 15.37 -603.1/

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

P5XC5H9-1E+H = CH3+C4H7 2.00E+21 -2.00 11000.0 ! Estimated JetSurF 2.0

P5XC5H9-1E(+M) = C2H4+aC3H5(+M) 4.57E+12 0.13 24386.4 ! Ref S5XC6H11-1E(+M) = C3H6+aC3H5(+M)

LOW / 2.50E-31 14.57 -578.8 /

TROE / -13.17 268 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C5H8-14E+H(+M) = P5XC5H9-1E(+M) 1.33E+13 0.00 3260.7 ! Ref to C3H6+H(+M) = nC3H7(+M)

LOW / 6.26E+38 -6.66 7000.0/

TROE / 1.000 1000.0 1310.0 48097.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S4XC5H9-1E = C5H8-13E+H 1.27E+24 -4.75 23777 ! Ref to C4H7 = C4H6+H

PLOG / 0.033 1.27E+24 -4.75 23777/

PLOG / 0.066 1.38E+26 -5.221 25729/

PLOG / 0.132 1.75E+28 -5.709 27764/

PLOG / 0.197 3.16E+29 -6.003 28985/

PLOG / 0.263 2.69E+30 -6.222 29890/

PLOG / 1.0 2.48E+53 -12.30 52000/

PLOG / 10 1.85E+48 -10.50 51770/

C3H6+C2H3 = S4XC5H9-1E 1.23E+35 -7.76 9930.0 ! Ref to C2H4+C2H3=C4H7

PLOG / 0.033 6.15E+34 -7.76 9930 /

PLOG / 0.1 1.23E+35 -7.76 9930 /

PLOG / 1.0 7.93E+38 -8.47 14220/

PLOG / 10 2.99E+36 -7.40 15480/

S4XC5H9-2E(+M) = C5H8-13E+H(+M) 4.70E+08 1.32 44697.6 ! Ref to SAXC4H7 = C4H6 + H

LOW / 4.6E-37 15.37 -603.1/

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

P5XC5H9-2E = C5H8-13E+H 1.27E+24 -4.75 23777 ! Ref to C4H7 = C4H6+H

PLOG / 0.033 1.27E+24 -4.75 23777/

PLOG / 0.066 1.38E+26 -5.221 25729/

PLOG / 0.132 1.75E+28 -5.709 27764/

PLOG / 0.197 3.16E+29 -6.003 28985/

PLOG / 0.263 2.69E+30 -6.222 29890/

PLOG / 1.0 2.48E+53 -12.30 52000/

PLOG / 10 1.85E+48 -10.50 51770/

CH3CHCH+C2H4 = P5XC5H9-2E 1.23E+35 -7.76 9930 ! Ref to C2H4+C2H3 = C4H7

PLOG / 0.033 6.15E+34 -7.76 9930 /

PLOG / 0.1 1.23E+35 -7.76 9930 /

PLOG / 1.0 7.93E+38 -8.47 14220/

PLOG / 10 2.99E+36 -7.40 15480/

C4H6+CH3(+M) = P4XC4H6-1E3M(+M) 9.60E+10 0.00 8003.6 ! Ref to C3H6+CH3(+M) = iC4H9(+M)

LOW / 1.30E+28 -4.27 2431.1 /

TROE / 0.565 60000.0 534.2 3007.2 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

P4XC4H6-1E3M = C4H5-13E2M+H 6.35E+23 -4.75 23777 ! Ref to C4H7 = C4H6+H /2

PLOG / 0.033 6.35E+23 -4.75 23777/

PLOG / 0.066 6.90E+25 -5.221 25729/

PLOG / 0.132 8.75E+27 -5.709 27764/

PLOG / 0.197 1.58E+29 -6.003 28985/

PLOG / 0.263 1.35E+30 -6.222 29890/

PLOG / 1.0 1.24E+53 -12.30 52000/

PLOG / 10 9.25E+47 -10.50 51770/

C2H3+C3H6 = P4XC4H6-1E3M 1.23E+35 -7.76 9930 ! Ref to C2H4+C2H3 = C4H7

PLOG / 0.033 6.15E+34 -7.76 9930/

PLOG / 0.1 1.23E+35 -7.76 9930/

PLOG / 1.0 7.93E+38 -8.47 14220/

PLOG / 10 2.99E+36 -7.40 15480/

```
P4XC4H6-1E2M = C4H5-13E2M+H 1.27E+24 -4.75 23777 ! Ref to C4H7 = C4H6+H
PLOG / 0.033 1.27E+24 -4.75 23777/
PLOG / 0.066 1.38E+26 -5.221 25729/
PLOG / 0.132 1.75E+28 -5.709 27764/
PLOG / 0.197 3.16E+29 -6.003 28985/
PLOG / 0.263 2.69E+30 -6.222 29890/
PLOG / 1.0 2.48E+53 -12.30 52000/
PLOG / 10 1.85E+48 -10.50 51770/
CH3CCH2+C2H4 = P4XC4H6-1E2M 1.23E+35 -7.76 9930.0 ! Ref to C2H4+C2H3 = C4H7
PLOG / 0.033 6.15E+34 -7.76 9930/
PLOG / 0.1 1.23E+35 -7.76 9930/
PLOG / 1.0 7.93E+38 -8.47 14220/
PLOG / 10 2.99E+36 -7.40 15480/
!reactions of C5H10-1E
S4XC5H9-1E+H(+M) = C5H10-1E(+M) 2.40E+13 0.00 0.0 ! = iC3H7+H
LOW / 1.70E+58 -12.08 11263.7 /
TROE / 0.649 1213.1 1213.1 13369.7 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S3XC5H9-1E+H(+M)=C5H10-1E(+M) 2.00E+14 0.00 0.0 ! (aC3H5+H)
LOW / 1.33E+60 -12.00 5967.8 /
TROE / 0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/ P5XC5H9-1E+H(+M) = C5H10-1E(+M) 3.60E+13 0.00 0.0 ! =nC3H7+H JetSurF 2.0
LOW / 3.01E+48 -9.32 5833.6 /
TROE / 0.498 1314.0 1314.0 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C5H10-1E=aC3H5+C2H5 1.07E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7 !
PLOG / 0.039 1.07E+80 -19.33 95177/
PLOG / 0.066 2.50E+68 -16.040 86832/
PLOG / 0.132 1.480E+59 -13.261 82596/
PLOG / 0.197 2.43E+61 -13.999 82637/
PLOG / 0.263 3.75E+59 -13.427 82179/
PLOG / 1.0E+5 1.46E+16 0.00 69120/
C5H10-1E=C4H7+CH3 2.7E+80 -1.93E+01 1.07E+05 ! Ref to C6H12-1E=C4H7+C2H5
PLOG / 0.033 2.7E+80 -19.331 107015/
PLOG / 0.066 6.27E+68 -16.040 98670/
PLOG / 0.132 3.70E+59 -13.261 94434/
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PLOG / 0.197 6.08E+61 -13.999 94475/
PLOG / 0.263 9.38E+59 -13.427 94017/
PLOG / 1.0E+5 1.46E+16 0 81020/
C5H10-1E = C3H6+C2H4 8.0E+05 1.81 53454 !
PLOG / 0.039 8.0E+05 1.81 53454/ ! 1.62E+06 /20 EST
PLOG / 1 1.62E+06 1.81 53454/ ! 08/TSAwip JetSurF 2.0
C5H10-1E+H = S3XC5H9-1E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571
C5H10-1E+CH3 = S3XC5H9-1E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
C5H10-1E+H = S4XC5H9-1E+H2 1.3E06 2.4 4471 ! secondary LLNL-MI-407571
C5H10-1E+CH3 = S4XC5H9-1E+CH4 1.51 3.46 5481 ! secondary LLNL-MI-407571
C5H10-1E+H = P5XC5H9-1E+H2 6.651E05 2.54 6756 ! primary LLNL-MI-407571
C5H10-1E+CH3 = P5XC5H9-1E+CH4 4.521E-1 3.65 7154 ! primary LLNL-MI-407571
! reactions of C5H10-2E
SAXC4H7+CH3(+M)=C5H10-2E(+M) 1.00E+14 -0.32 -262. ! Ref to aC3H5+CH3=C4H8-1
LOW /3.51E+60 -12.97 6000./
TROE / 0.896 60000 1606 6118/
H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/
C2H5+CH3CHCH(+M) = C5H10-2E(+M) 1.50E+13 0.00 0.0 ! Ref to C2H5+C2H3=C4H8-1
LOW /1.55E+56 -11.79 8984.5/
TROE /0.198 2277.9 60000.0 5723.2 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
P5XC5H9-2E+H(+M) = C5H10-2E(+M) 3.60E+13 0.00 0.0 ! Ref to C4H7+H = C4H8-1
LOW / 3.01E+48 -9.32 5833.6 /
TROE / 0.498 1314.0 1314.0 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S4XC5H9-2E+H(+M) = C5H10-2E(+M) 2.00E+14 0.00 0.0 ! Ref to SAXC4H7+H = C4H8-1
LOW / 2.66E+60 -12.00 5967.8 /
H2/2/ CH4/2/ C2H6/3/
S3XC5H9-1E+H(+M) = C5H10-2E(+M) 2.00E+14 0.00 0.0 ! Ref to aC3H5+H = C3H6
LOW / 1.33E+60 -12.00 5967.8 /
TROE/ 0.020 1096.6 1096.6 6859.5 /
```

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C5H10-2E+H = S3XC5H9-1E+H2 1.73E5 2.5 2492 ! allylp LLNL-MI-407571

C5H10-2E+CH3 = S3XC5H9-1E+CH4 2.2098 3.5 5675 ! allylp LLNL-MI-407571

C5H10-2E+H = S4XC5H9-2E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571

C5H10-2E+CH3 = S4XC5H9-2E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C5H10-2E+H = P5XC5H9-2E+H2 6.651E05 2.54 6756 ! primary LLNL-MI-407571

C5H10-2E+CH3 = P5XC5H9-2E+CH4 4.521E-1 3.65 7154 ! primary LLNL-MI-407571

! reactions of C5H11

PXC5H11(+M) = C2H4+nC3H7(+M) 1.00E+13 0.00 28366.4 ! 1998 TSA JetSurF 2.0

LOW / 7.10E-35 15.411 -600.0/

TROE / -5.91 333.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

PXC5H11(+M) = S2XC5H11(+M) 1.00E+12 0.00 22453.1 ! 1998 TSA JetSurF 1.1

LOW / 2.00E-26 12.833 -600.7/

TROE / -10.14 307.0 28.0 5000000 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C5H10-1E+H(+M) = PXC5H11(+M) 1.33E+13 0.00 3260.7 ! Ref C3H6+H(+M) = nC3H7(+M)

LOW / 6.26E+38 -6.66 7000.0 /

TROE / 1.000 1000.0 1310.0 48097.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

PXC5H11+H = nC3H7+C2H5 3.40E+18 -1.33 5386.0 ! =(nC3H7+H) 0.1 atm JetSurF 2.0

PXC5H11+H = C5H10-1E+H2 1.80E+12 0.00 0.0 ! =(nC3H7+H) JetSurF 2.0

PXC5H11+CH3 = C5H10-1E+CH4 1.10E+13 0.00 0.0 ! =(nC3H7+CH3) JetSurF 2.0

S2XC5H11(+M) = C3H6+C2H5(+M) 8.00E+12 0.00 27392.8 ! 1998 TSA JetSurF 2.0

LOW / 3.70E-33 14.91 -600.0 /

TROE / -6.53 333.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C5H10-1E+H(+M) = S2XC5H11(+M) 1.33E+13 0.00 1559.8 ! Ref C3H6+H(+M) = iC3H7(+M) USC Mech II

LOW / 8.70E+42 -7.50 4721.8/

TROE / 1.000 1000.0 645.4 6844.3 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S2XC5H11+H = nC3H7+C2H5 5.90E+23 -2.81 10009.0 ! =(iC3H7+H) JetSurF 2.0

S2XC5H11+H = C5H10-1E+H2 3.20E+12 0.00 0.0 ! =(iC3H7+H) JetSurF 2.0

S2XC5H11+CH3 = CH4+C5H10-1E 2.20E+14 -0.68 0.0 ! =(iC3H7+CH3) JetSurF 2.0

S3XC5H11(+M) = C4H8-1+CH3(+M) 1.80E+13 0.00 29348.0 ! 1998 TSA JetSurF 2.0

LOW / 4.00E-39 16.782 -600.4/

TROE / -7.03 314.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

!!!C6

! C6H10 C6H9 C6H8 reactions

lC5H7(+M)+CH3 = C6H10-13E(+M) 1.00E+14 -0.32 -262.3 ! 1991 TSA JetSurF 2.0

LOW / 3.91E+60 -12.81 6250.0 /

TROE / 0.104 1606.0 60000.0 6118.4 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C6H10-13E+H = C4H8-1+C2H3 1.46E+30 -4.34 21647.0 ! =(C4H6+H) JetSurF 2.0

C6H10-13E + H = S2XC6H9-13E + H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571

C6H10-13E + CH3 = S2XC6H9-13E + CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C6H10-15E = aC3H5+aC3H5 1.07E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

C6H10-15E + H = S3XC6H9-15E + H2 6.752E05 2.36 207 ! (ax4) allyls LLNL-MI-407571

C6H10-15E + CH3 = S3XC6H9-15E + CH4 7.38 3.31 4002 ! (ax4) allyls LLNL-MI-407571

S2XC6H9-13E(+M) = C6H8-135E+H(+M) 4.70E+08 1.32 44697.6 ! Ref to SAXC4H7

LOW / 4.6E-37 15.37 -603.1 /

```
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
S3XC6H9-15E = C6H8-135E+H 1.27E+24 -4.75 23777 ! Ref to C4H7 = C4H6+H
PLOG / 0.033 1.27E+24 -4.75 23777/
PLOG / 0.066 1.38E+26 -5.221 25729/
PLOG / 0.132 1.75E+28 -5.709 27764/
PLOG / 0.197 3.16E+29 -6.003 28985/
PLOG / 0.263 2.69E+30 -6.222 29890/
PLOG / 1.0 2.48E+53 -12.30 52000/
PLOG / 10 1.85E+48 -10.50 51770/
C4H6+C2H3 = S3XC6H9-15E 1.23E+35 -7.76 9930 ! Ref to C2H4+C2H3 = C4H7
PLOG / 0.039 6.15E+34 -7.76 9930/
PLOG / 0.1 1.23E+35 -7.76 9930/
PLOG / 1.0 7.93E+38 -8.47 14220/
PLOG / 10 2.99E+36 -7.40 15480/
C2H3 + nC4H5 = C6H8-135E 7.00E+57 -13.82 17629. ! Ref to C2H3+C2H3=C4H6
PLOG / 0.026 7.00E+57 -13.82 17629/
PLOG / 0.118 1.50E+52 -11.97 16056/
PLOG / 1.0 1.50E+42 -8.84 12483/
P1XC6H9-13E = C6H8-135E+H 1.27E+24 -4.75 23777 ! Ref to C4H7 = C4H6+H
PLOG / 0.033 1.27E+24 -4.75 23777/
PLOG / 0.066 1.38E+26 -5.221 25729/
PLOG / 0.132 1.75E+28 -5.709 27764/
PLOG / 0.197 3.16E+29 -6.003 28985/
PLOG / 0.263 2.69E+30 -6.222 29890/
PLOG / 1.0 2.48E+53 -12.30 52000/
PLOG / 10 1.85E+48 -10.50 51770/
C2H4+nC4H5=P1XC6H9-13E 1.23E+35 -7.76 9930 ! Ref to C2H4+C2H3 = C4H7
PLOG / 0.039 6.15E+34 -7.76 9930/
PLOG / 0.1 1.23E+35 -7.76 9930/
PLOG / 1.0 7.93E+38 -8.47 14220/
PLOG / 10 2.99E+36 -7.40 15480/
C6H8-135E+H = C2H4+nC4H5 1.46E+30 -4.34 21647 ! Ref to C4H6+H = C2H4+C2H3
C6H8-135E+H = C2H3+C4H6 1.46E+30 -4.34 21647 ! Ref to C4H6+H = C2H4+C2H3
```

! cC6H10 cC6H9 cC6H8 reactions

cC6H10 = C4H6+C2H4 5.0E+78 -18.94 98386 ! EST

PLOG / 0.039 5.0E+78 -18.94 98386/

PLOG / 0.197 2.60E+70 -16.36 95510/

PLOG / 1.0 3.81E+25 -3.58 64034/

PLOG / 1.0E+5 8.31E+13 0.387 64116/

S3XcC6H9-1E+H(+M) = cC6H10(+M) 2.66E+14 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *4/3

LOW / 1.77E+60 -12.00 5967.8 /

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

cC6H10+H = S3XcC6H9-1E+H2 6.752E05 2.36 207 ! (ax4) allyls LLNL-MI-407571

cC6H10 + CH3 = S3XcC6H9-1E+CH4 7.38 3.31 4002 ! (ax4) allyls LLNL-MI-407571

S3XcC6H9-1E = cC6H8-13E+H 2.67E+12 0.71 49792.2 ! JetSurF 2.0

PLOG / 0.039 1.62E+57 -13.03 66036/ ! 2011 Li et al.

PLOG / 1.0 2.67E+12 0.71 49792.2/ ! JetSurF 2.0

S3XcC6H9-1E=P1XC6H9-13E 1.30E+13 0.00 35900 ! 2003 Dayma et al.

PLOG / 0.039 5.36E+50 -11.92 48276/ ! 2011 Li et al.

PLOG / 1.0 1.30E+13 0.00 35900/ ! 2003 Dayma et al.

S3XcC6H9-1E+H = cC6H8-13E+H2 1.80E+13 0.00 0.0 ! Ref to SAXC4H7+H

cC6H8-13E+H = S1XcC6H7-24E+H2 6.752E05 2.36 207 ! (ax4) allyls LLNL-MI-407571

cC6H8-13E + CH3 = S1XcC6H7-24E+CH4 7.38 3.31 4002 ! (ax4) allyls LLNL-MI-407571

S1XcC6H7-24E=A1+H 6.76E+11 0.78 30230 !

PLOG / 0.039 3.40E+10 0.78 30230/ ! /20 EST

PLOG / 1.0 6.76E+11 0.78 30230/ ! JetSurF 2.0

S1XcC6H7-24E+H = A1+H2 1.80E+13 0.00 0.0 ! Ref to SAXC4H7+H

! C6H11 reactions

P1XC6H11-1E(+M) = C4H7+C2H4(+M) 3.98E+12 0.12 27571.6 ! JetSurF 2.0

LOW / 3.30E-43 18.35 -602.5 /

TROE / -13.87 227 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C6H10-15E+H(+M) = P1XC6H11-1E(+M) 1.33E+13 0.00 3260.7 ! Ref to C3H6+H(+M) = nC3H7(+M)

LOW / 6.26E+38 -6.66 7000.0/

TROE / 1.000 1000.0 1310.0 48097.0 /

```
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
P1XC6H11-1E(+M) = S3XC6H11-1E(+M) 1.55E+02 2.83 15566.2 ! JetSurF 2.0
LOW / 1.50E-30 14.56 -602.4 /
TROE / -13.59 214 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S3XC6H11-1E(+M) = C4H6+C2H5(+M) 3.39E+11 0.66 32262.9 ! JetSurF 2.0
LOW / 4.00E-42 18.05 -602.6 /
TROE / -18.50 246 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S3XC6H11-1E(+M) = C6H10-13E+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7 = C4H6 + H *2/3
LOW / 3.07E-37 15.37 -603.1/
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
S3XC6H11-1E+H=C6H10-13E+H2 1.60E+12 0.00 0.0 ! Ref to iC3H7+H /2
S3XC6H11-1E+CH3=C6H10-13E+CH4 4.7E+10 0.68 0.0 ! Ref to iC3H7+CH3 /2
S5XC6H11-1E(+M) = C3H6+aC3H5(+M) 4.57E+12 0.13 24386.4 ! JetSurF 2.0
LOW / 2.50E-31 14.57 -578.8 /
TROE / -13.17 268 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C6H10-15E+H(+M) = S5XC6H11-1E(+M) 1.33E+13 0.00 1559.8 ! Ref to C4H8-1+H(+M) = sC4H9(+M)
LOW / 8.70E+42 -7.50 4721.8 /
TROE / 1.000 1000.0 645.4 6844.3 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S4XC6H11-1E(+M) = C5H8-14E+CH3(+M) 8.13E+10 0.78 29648.0 ! 2007 TSA JetSurF 2.0
LOW / 4.00E-39 16.782 -600.4 /
TROE / -7.03 314.0 28.0 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S4XC6H11-1E = C6H10-13E+H 1.27E+24 -4.75 23777 ! Ref to C4H7 = C4H6+H
PLOG / 0.033 1.27E+24 -4.75 23777/
PLOG / 0.066 1.38E+26 -5.221 25729/
PLOG / 0.132 1.75E+28 -5.709 27764/
PLOG / 0.197 3.16E+29 -6.003 28985/
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PLOG / 0.263 2.69E+30 -6.222 29890/
PLOG / 1.0 2.48E+53 -12.30 52000/
PLOG / 10 1.85E+48 -10.50 51770/
S4XC6H11-1E+H = nC3H7+aC3H5 2.00E+21 -2.00 11000 ! Ref to C4H7+H
S4XC6H11-1E+H = C6H10-13E+H2 1.80E+12 0.00 0.0 ! Ref to C4H7+H
S4XC6H11-1E+CH3 = C6H10-13E+CH4 1.10E+13 0.00 0.0 ! Ref to C4H7+CH3
P1XCH2cC5H9=P1XC6H11-1E 8.92E+18 -2.94 19897 ! Ref to PXCH2cC6H11=P7XC7H13-1E
PLOG / 0.039 8.92E+18 -2.94 19897 /
PLOG / 0.197 6.83E+22 -3.82 23511 /
PLOG / 1.000 1.56E+29 -5.39 29211 /
PLOG / 10.000 4.15E+37 -7.44 37753 /
PLOG / 100.000 1.92E+39 -7.58 42286 /
PLOG / 1.0E+5 2.53E+13 0.16 29785 /
P1XCH2cC5H9=CH2cC5H8+H 8.14E+14 -2.42 21719 ! Ref to PXCH2cC6H11=CH2cC6H10
PLOG / 0.039 8.14E+14 -2.42 21719 /
PLOG / 0.197 1.23E+20 -3.61 26095 /
PLOG / 1.000 1.18E+28 -5.58 32946 /
PLOG / 10.000 1.31E+39 -8.28 43693 /
PLOG / 100.000 4.67E+42 -8.87 50298 /
PLOG / 1.0E+5 1.60E+11 0.59 35447 /
P1XCH2cC5H9(+M) = S3XcC5H81M(+M) 6.61E+01 2.85 21082.1 ! 08/TSAwip JetSurF 2.0
LOW / 1.10E-36 16.12 -602.5 /
TROE / -21.57 225 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S3XcC5H81M=P5XC5H8-1E4M 1.21E+18 -2.84 19903 ! Ref to S3XMCH=P6XC6H10-1E4M
PLOG / 0.039 1.21E+18 -2.84 19903 /
PLOG / 0.197 7.98E+21 -3.70 23365 /
PLOG / 1.000 2.52E+28 -5.31 28978 /
PLOG / 10.000 8.05E+37 -7.66 38033 /
PLOG / 100.000 6.13E+42 -8.70 44718 /
PLOG / 1.0E+5 1.68E+13 0.21 31241 /
S3XcC5H81M=S5XC6H11-1E 5.23E+18 -2.93 19555 ! Ref to S3XMCH=S6XC7H13-1E
PLOG / 0.039 5.23E+18 -2.93 19555 /
PLOG / 0.197 2.06E+22 -3.73 22876 /
PLOG / 1.000 3.29E+28 -5.27 28275 /
PLOG / 10.000 3.31E+37 -7.49 36918 /
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PLOG / 100.000 8.80E+41 -8.42 43157 /
PLOG / 1.0E+5 2.55E+13 0.17 30061 /
P5XC5H8-1E4M(+M) = aC3H5+C3H6(+M) 5.37E+12 0.12 23947.3 ! 08/TSAwip JetSurF 2.0
LOW / 4.90E-31 14.54 -578.8 /
TROE / -11.90 267 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
! cC6H11 reactions
cC6H11=P1XC6H11-1E 1.26E+22 -3.85 22627 ! Ref to S4XMCH=P1XCH2C6H11-1E
PLOG / 0.039 1.26E+22 -3.85 22627 /
PLOG / 0.197 3.57E+26 -4.89 26638 /
PLOG / 1.000 2.59E+32 -6.32 32020 /
PLOG / 10.000 2.07E+41 -8.51 40814 /
PLOG / 100.000 5.79E+44 -9.15 46530 /
PLOG / 1.0E+5 3.87E+13 0.20 31782 /
cC6H11=cC6H10+H 8.38E+20 -3.63 23771 ! Ref to S4XMCH=MCH-3E+H
PLOG / 0.039 8.38E+20 -3.63 23771 /
PLOG / 0.197 8.32E+25 -4.80 28120 /
PLOG / 1.000 5.73E+32 -6.47 34206 /
PLOG / 10.000 1.37E+43 -9.02 44242 /
PLOG / 100.000 7.21E+47 -9.98 51272 /
PLOG / 1.0E+5 3.78E+12 0.63 34881 /
cC6H11+H = cC6H10+H2 3.60E+12 0.00 0.0 ! Ref to nC3H7+H *2
cC6H11+CH3 = cC6H10+CH4 2.20E+13 -0.32 0.0 ! Ref to nC3H7+CH3 *2
!C6H12-1E reactions
P1XC6H11-1E+H(+M) = C6H12-1E(+M) 3.60E+13 0.00 0.0 ! = nC3H7+H
LOW / 3.01E+48 -9.32 5833.6 /
TROE / 0.498 1314.0 1314.0 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S5XC6H11-1E+H(+M) = C6H12-1E(+M) 2.40E+13 0.00 0.0 ! = iC3H7+H
LOW / 1.70E+58 -12.08 11263.7/
TROE / 0.649 1213.1 1213.1 13369.7 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S4XC6H11-1E+H(+M) = C6H12-1E(+M) 2.40E+13 0.00 0.0 ! = iC3H7+H
LOW / 1.70E+58 -12.08 11263.7/
TROE / 0.649 1213.1 1213.1 13369.7 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S3XC6H11-1E+H(+M)=C6H12-1E(+M) 2.00E+14 0.00 0.0 ! = (aC3H5+H)
LOW / 1.33E+60 -12.00 5967.8/
```

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C6H12-1E=aC3H5+nC3H7 1.07E+80 -19.33 95177 !

PLOG / 0.039 1.07E+80 -19.33 95177/ ! 2009 Kiefer et al.

PLOG / 0.066 2.50E+68 -16.040 86832/ ! 2009 Kiefer et al.

PLOG / 0.132 1.480E+59 -13.261 82596/ ! 2009 Kiefer et al.

PLOG / 0.197 2.43E+61 -13.999 82637/ ! 2009 Kiefer et al.

PLOG / 0.263 3.75E+59 -13.427 82179/ ! 2009 Kiefer et al.

PLOG / 1.0E+5 1.46E+16 0.00 69120/ ! 2009 Kiefer et al.

C6H12-1E=C4H7+C2H5 2.7E+80 -19.331 107015

PLOG / 0.033 2.7E+80 -19.331 107015/ ! 2009 Kiefer et al.

PLOG / 0.066 6.27E+68 -16.040 98670/ ! 2009 Kiefer et al.

PLOG / 0.132 3.70E+59 -13.261 94434/ ! 2009 Kiefer et al.

PLOG / 0.197 6.08E+61 -13.999 94475/ ! 2009 Kiefer et al.

PLOG / 0.263 9.38E+59 -13.427 94017/ ! 2009 Kiefer et al.

PLOG / 1.0E+5 1.46E+16 0.0 81020/ ! EST

C6H12-1E = C3H6+C3H6 7.08E+06 1.65 53752.0 !

PLOG / 0.039 3.54E+05 1.65 53752.0 / ! /20 EST

PLOG / 1.0 7.08E+06 1.65 53752.0 / ! JetSurF 2.0

C6H12-1E+H=S3XC6H11-1E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571

C6H12-1E+CH3=S3XC6H11-1E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C6H12-1E+H=S5XC6H11-1E+H2 1.3E06 2.4 4471 ! secondary LLNL-MI-407571

C6H12-1E+CH3=S5XC6H11-1E+CH4 1.51 3.46 5481 ! secondary LLNL-MI-407571

C6H12-1E+H=S4XC6H11-1E+H2 1.3E06 2.4 4471 ! secondary LLNL-MI-407571

C6H12-1E+CH3=S4XC6H11-1E+CH4 1.51 3.46 5481 ! secondary LLNL-MI-407571

C6H12-1E+H = P1XC6H11-1E+H2 6.651E05 2.54 6756 ! primary LLNL-MI-407571

C6H12-1E+CH3 = P1XC6H11-1E+CH4 4.521E-1 3.65 7154 ! primary LLNL-MI-407571

! cC6H12 reactions

cC6H11+H(+M)=cC6H12(+M) 4.80E+13 0.00 0.0 ! =(iC3H7+H) JetSurF 2.0

LOW / 1.70E+58 -12.08 11263.7/

TROE / 0.649 1213.1 1213.1 13369.7 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

cC6H12=C6H12-1E 1.33E+137 -34.70 162775 ! 2009 Kiefer et al.

PLOG / 0.039 1.33E+137 -34.70 162775/ ! /1.5

PLOG / 0.066 5.96E+139 -35.26 166598/ !

PLOG / 0.263 1.82E+143 -35.99 172904/ !

PLOG / 1.0E+5 8.76E+17 0.00 91940 / !

cC6H12+H=cC6H11+H2 2.70E+10 1.385 8229 ! 2009 Kiefer et al.

cC6H12+CH3=cC6H11+CH4 9.06E+00 3.46 5480 ! Ref to C3H8+CH3=iC3H7+CH4 *6

! CH2cC6H6-25E and CH2cC6H6-35E reactions

A1CH2+H(+M)=CH2cC6H6-35E(+M) 4.98E11 0.611 -436 ! oit 2007 Klippenstein

LOW / 1.34E52 -10.3 -3910 /

TROE / 0.01 1 -1300 50000/

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

A1CH2+H(+M)=CH2cC6H6-25E(+M) 6.44E12 0.245 -333 ! pit 2007 Klippenstein

LOW / 2.62E45 -8.59 -11590/

TROE / 0.025 1 -5000 50000/

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

CH2cC6H6-35E+H=A1CH2+H2 6.47E00 3.98 3394.0 ! Ref to A1CH3

CH2cC6H6-35E+CH3=A1CH2+CH4 3.160E+11 0.000 9500.00 ! Ref to A1CH3

! cC7H9 reactions

S5XMCH-13E(+M)=A1CH3+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1 /

TROE /-51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

S6XMCH-13E(+M)=A1CH3+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1 /

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

S3XMCH-15E(+M)=A1CH3+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1 /

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

S4XMCH-15E(+M)=A1CH3+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1 /

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

S2XMCH-35E(+M)=A1CH3+H(+M) 1.56E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *1/3

LOW / 1.53E-37 15.37 -603.1 /

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

T1XMCH-35E(+M)=A1CH3+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1 /

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

T1XMCH-35E(+M)=CH2cC6H6-35E+H(+M) 4.70E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M)

LOW / 4.6E-37 15.37 -603.1 /

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

CH2S4XcC6H7-5E(+M)=CH2cC6H6-35E+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1 /

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

CH2S2XcC6H7-5E(+M)=CH2cC6H6-25E+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1 /

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

!!!!!C7

! cC7H10 reactions

MCH-13E+H = S5XMCH-13E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571

MCH-13E+CH3= S5XMCH-13E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

S5XMCH-13E+H(+M)=MCH-13E(+M) 1.33E+14 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M *2/3

LOW /0.89E+60 -12.00 5967.8/

TROE /0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S6XMCH-13E+H(+M)=MCH-13E(+M) 1.33E+14 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M *2/3

LOW /0.89E+60 -12.00 5967.8/

TROE /0.020 1096.6 1096.6 6859.5 /

```
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
MCH-13E+H = S6XMCH-13E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571
MCH-13E+CH3= S6XMCH-13E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
MCH-13E+H = CH2S4XcC6H7-5E+H2 1.73E5 2.5 2492 ! allylp LLNL-MI-407571
MCH-13E+CH3= CH2S4XcC6H7-5E+CH4 2.2098 3.5 5675 ! allylp LLNL-MI-407571
CH2S4XcC6H7-5E+H(+M)=MCH-13E(+M) 2.00E+14 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M)
LOW /1.33E+60 -12.00 5967.8/
TROE /0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
MCH-15E+H = S3XMCH-15E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571
MCH-15E+CH3= S3XMCH-15E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
S3XMCH-15E+H(+M)=MCH-15E(+M) 1.33E+13 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *2/3
LOW /0.89E+59 -12.00 5967.8/
TROE /0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
MCH-15E+H = S4XMCH-15E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571
MCH-15E+CH3= S4XMCH-15E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
S4XMCH-15E+H(+M)=MCH-15E(+M) 1.33E+13 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *2/3
LOW /0.89E+59 -12.00 5967.8/
TROE / 0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
MCH-15E+H = CH2S2XcC6H7-5E+H2 1.73E5 2.5 2492 ! allylp LLNL-MI-407571
MCH-15E+CH3= CH2S2XcC6H7-5E+CH4 2.2098 3.5 5675 ! allylp LLNL-MI-407571
CH2S2XcC6H7-5E+H(+M)=MCH-15E(+M) 2.00E+14 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M)
LOW /1.33E+60 -12.00 5967.8/
TROE /0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S2XMCH-35E+H(+M)=MCH-35E(+M) 1.33E+13 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *2/3
```

LOW / 0.89E+59 -12.00 5967.8 /

TROE / 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

T1XMCH-35E+H(+M)=MCH-35E(+M) 0.67E+13 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *1/3

LOW / 0.44E+59 -12.00 5967.8 /

TROE/ 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S1XcC6H7-24E+CH3(+M)=MCH-35E(+M) 1.00E+14 -0.32 -262. ! Ref to aC3H5+CH3(+M)=C4H8-1(+M)

LOW / 3.51E+60 -12.97 6000./

TROE / 0.896 60000 1606 6118/

H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/

CH2cC6H8-2E+H = CH2S4XcC6H7-5E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571

CH2cC6H8-2E+CH3= CH2S4XcC6H7-5E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

CH2S4XcC6H7-5E+H(+M)=CH2cC6H8-2E(+M) 1.33E+13 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *2/3

LOW / 0.89E+59 -12.00 5967.8 /

TROE/ 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

CH2cC6H8-2E+H = CH2S2XcC6H7-5E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571

CH2cC6H8-2E+CH3= CH2S2XcC6H7-5E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

CH2S2XcC6H7-5E+H(+M)=CH2cC6H8-2E(+M) 1.33E+13 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *2/3

LOW / 0.89E+59 -12.00 5967.8 /

TROE/ 0.020 1096.6 1096.6 6859.5 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

!C6H7-135E2M,C6H7-135E3M, C7H10-135E reactions

C6H7-135E2M+H = C4H6+CH3CCH2 1.46E+30 -4.34 21647 ! Ref to C4H6+H = C2H4+C2H3

C6H7-135E2M+H = S4XC4H4-13E2M+C2H4 1.46E+30 -4.34 21647 ! Ref to C4H6+H = C2H4+C2H3

C6H7-135E2M+H = C6H8-135E+CH3 8.80E+16 -1.05 6461.0 ! Ref to C3H6+H = C2H4+CH3

C6H7-135E2M+H = C3H6+nC4H5 1.46E+30 -4.34 21647 ! Ref to C4H6+H = C2H4+C2H3

C6H7-135E2M+H = C4H5-13E2M+C2H3 1.46E+30 -4.34 21647 ! Ref to C4H6+H = C2H4+C2H3

C6H7-135E3M+H = T4XC5H7-13E+C2H4 1.46E+30 -4.34 21647 ! Ref to C4H6+H = C2H4+C2H3

C6H7-135E3M+H = S1XC4H4-13E2M+C2H4 1.46E+30 -4.34 21647 ! Ref to C4H6+H = C2H4+C2H3

C6H7-135E3M+H = C4H5-13E2M+C2H3 1.46E+30 -4.34 21647 ! Ref to C4H6+H = C2H4+C2H3

C6H7-135E3M+H = C5H8-13E+C2H3 1.46E+30 -4.34 21647 ! Ref to C4H6+H = C2H4+C2H3

C6H7-135E3M+H = C6H8-135E+CH3 8.80E+16 -1.05 6461.0 ! Ref to C3H6+H = C2H4+CH3

C7H10-135E+H = S1XC5H7-13E+C2H4 1.46E+30 -4.34 21647 ! Ref to C4H6+H = C2H4+C2H3

C7H10-135E+H = C4H6+CH3CHCH 1.46E+30 -4.34 21647 ! Ref to C4H6+H = C2H4+C2H3

C7H10-135E+H = C6H8-135E+CH3 8.80E+16 -1.05 6461.0 ! Ref to C3H6+H = C2H4+CH3

C7H10-135E+H = C5H8-13E+C2H3 1.46E+30 -4.34 21647 ! Ref to C4H6+H = C2H4+C2H3

C7H10-135E+H = nC4H5+C3H6 1.46E+30 -4.34 21647 ! Ref to C4H6+H = C2H4+C2H3

! cyclic C7H11 reactions

S3XMCH-1E(+M)=MCH-13E+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW/ 3.07E-37 15.37 -603.1/

TROE /-51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

S2XMCH-5E(+M)=MCH-15E+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1/

TROE/ -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

T1XMCH-2E(+M)=MCH-15E+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3

LOW / 3.07E-37 15.37 -603.1/

TROE/ -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

T1XMCH-2E(+M)=CH2cC6H8-2E+H(+M) 4.70E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M)

```
LOW / 4.60E-37 15.37 -603.1/
TROE/ -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
S2XMCH-3E(+M)=MCH-35E+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3
LOW/ 3.07E-37 15.37 -603.1/
TROE /-51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
S2XMCH-3E(+M)=MCH-13E+H(+M) 1.57E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *1/3
LOW/ 1.54E-37 15.37 -603.1/
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
S2XMCH-3E=cC6H8-13E+CH3 4.24E+21 -3.89 22867 ! Ref to S2XMCH=cC6H10+CH3
PLOG / 0.039 4.24E+21 -3.89 22867 / !
PLOG / 0.197 2.58E+22 -3.86 24360 / !
PLOG / 1.000 2.27E+28 -5.30 29571 / !
PLOG / 10.000 4.14E+38 -7.84 39088 / !
PLOG / 100.000 1.94E+45 -9.36 47105 / !
PLOG / 1.0E+5 6.35E+13 0.20 33524 / !
S5XMCH-3E(+M)=MCH-35E+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *2/3
LOW/ 3.07E-37 15.37 -603.1/
TROE / -51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
CH2S2XcC6H9(+M)=CH2cC6H8-2E+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M *2/3
LOW/ 3.07E-37 15.37 -603.1/
TROE /-51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
! chain C7H11 reactions
S3XC7H11-16E(+M) = C4H6+aC3H5(+M) 3.39E+11 0.66 32262.9 ! Ref to S3XC6H11-1E(+M) = C4H6+C2H5(+M)
LOW / 4.00E-42 18.05 -602.6 /
TROE / -18.50 246 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S3XC7H11-15E = C7H10-135E+H 1.27E+24 -4.75 23777 ! Ref to C4H7 = C4H6+H
PLOG / 0.033 1.27E+24 -4.75 23777/
PLOG / 0.066 1.38E+26 -5.221 25729/
```

PLOG / 0.132 1.75E+28 -5.709 27764/
PLOG / 0.197 3.16E+29 -6.003 28985/
PLOG / 0.263 2.69E+30 -6.222 29890/
PLOG / 1.0 2.48E+53 -12.30 52000/
PLOG / 10 1.85E+48 -10.50 51770/
C4H6+CH3CHCH = S3XC7H11-15E 1.23E+35 -7.76 9930.0 ! Ref to C2H4+C2H3 = C4H7
PLOG / 0.039 6.15E+34 -7.76 9930.0 /
PLOG / 0.1 1.23E+35 -7.76 9930.0 /
PLOG / 1.0 7.93E+38 -8.47 14220.0/
PLOG / 10 2.99E+36 -7.40 15480.0/
S4XC7H11-15E = C7H10-135E+H 1.27E+24 -4.75 23777 ! Ref to C4H7 = C4H6+H
PLOG / 0.033 1.27E+24 -4.75 23777 /
PLOG / 0.066 1.38E+26 -5.221 25729 /
PLOG / 0.132 1.75E+28 -5.709 27764 /
PLOG / 0.197 3.16E+29 -6.003 28985 /
PLOG / 0.263 2.69E+30 -6.222 29890 /
PLOG / 1.0 2.48E+53 -12.30 52000 /
PLOG / 10 1.85E+48 -10.50 51770 /
C5H8-13E+C2H3 = S4XC7H11-15E 1.23E+35 -7.76 9930.0 ! Ref to C2H4+C2H3 = C4H7
PLOG / 0.039 6.15E+34 -7.76 9930.0 /
PLOG / 0.1 1.23E+35 -7.76 9930.0 /
PLOG / 1.0 7.93E+38 -8.47 14220.0/
PLOG / 10 2.99E+36 -7.40 15480.0/
P7XC7H11-15E(+M) = C4H6+aC3H5(+M) 3.39E+11 0.66 32262.9 ! Ref to S3XC6H11-1E(+M) = C4H6+C2H5(+M)
LOW / 4.00E-42 18.05 -602.6 /
TROE / -18.50 246 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
T1XC6H8-15E3M = C6H7-135E3M+H 1.27E+24 -4.75 23777 ! Ref to C4H7 = C4H6+H
PLOG / 0.033 1.27E+24 -4.75 23777 /
PLOG / 0.066 1.38E+26 -5.221 25729 /
PLOG / 0.132 1.75E+28 -5.709 27764 /
PLOG / 0.197 3.16E+29 -6.003 28985 /
PLOG / 0.263 2.69E+30 -6.222 29890 /
PLOG / 1.0 2.48E+53 -12.30 52000 /
PLOG / 10 1.85E+48 -10.50 51770 /

C4H5-13E2M+C2H3 = T1XC6H8-15E3M 1.23E+35 -7.76 9930.0 ! Ref to C2H4+C2H3 = C4H7

PLOG / 0.039 6.15E+34 -7.76 9930.0 /

PLOG / 0.1 1.23E+35 -7.76 9930.0 /

PLOG / 1.0 7.93E+38 -8.47 14220.0/

PLOG / 10 2.99E+36 -7.40 15480.0/

S4XC6H8-15E3M (+M) = C6H8-135E+CH3 (+M) 3.39E+11 0.66 32262.9 ! Ref S3XC6H11-1E(+M) = C4H6+C2H5(+M)

LOW / 4.00E-42 18.05 -602.6 /

TROE / -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C5H8-13E+C2H3 = S4XC6H8-15E3M 1.23E+35 -7.76 9930.0 ! Ref to C2H4+C2H3 = C4H7

PLOG / 0.039 6.15E+34 -7.76 9930.0 /

PLOG / 0.1 1.23E+35 -7.76 9930.0 /

PLOG / 1.0 7.93E+38 -8.47 14220.0/

PLOG / 10 2.99E+36 -7.40 15480.0/

S4XC6H8-15E3M(+M) = C6H7-135E3M+H(+M) 1.57E+08 1.32 44697.6 ! Ref to SAXC4H7(+M) = C4H6+H(+M) *1/3

LOW/ 1.54E-37 15.37 -603.1 /

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

P1XCH2-3C6H9-15E(+M) = C4H6+aC3H5(+M) 4.57E+12 0.13 24386.4 ! Ref to S5XC6H11-1E(+M) = C3H6+aC3H5(+M)

LOW / 2.50E-31 14.57 -578.8/

TROE / -13.17 268 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S3XC6H8-15E2M = C6H7-135E2M+H 1.27E+24 -4.75 23777 ! Ref to C4H7 = C4H6+H

PLOG / 0.033 1.27E+24 -4.75 23777 /

PLOG / 0.066 1.38E+26 -5.221 25729 /

PLOG / 0.132 1.75E+28 -5.709 27764 /

PLOG / 0.197 3.16E+29 -6.003 28985 /

PLOG / 0.263 2.69E+30 -6.222 29890 /

PLOG / 1.0 2.48E+53 -12.30 52000 /

PLOG / 10 1.85E+48 -10.50 51770 /

C4H5-13E2M+C2H3 = S3XC6H8-15E2M 1.23E+35 -7.76 9930.0 ! Ref to C2H4+C2H3 = C4H7

PLOG / 0.039 6.15E+34 -7.76 9930.0 /

PLOG / 0.1 1.23E+35 -7.76 9930.0 /

PLOG / 1.0 7.93E+38 -8.47 14220.0/
PLOG / 10 2.99E+36 -7.40 15480.0/
S4XC6H8-15E2M = C6H7-135E2M+H 1.27E+24 -4.75 23777 ! Ref to C4H7 = C4H6+H
PLOG / 0.033 1.27E+24 -4.75 23777 /
PLOG / 0.066 1.38E+26 -5.221 25729 /
PLOG / 0.132 1.75E+28 -5.709 27764 /
PLOG / 0.197 3.16E+29 -6.003 28985 /
PLOG / 0.263 2.69E+30 -6.222 29890 /
PLOG / 1.0 2.48E+53 -12.30 52000 /
PLOG / 10 1.85E+48 -10.50 51770 /
C4H6+CH3CCH2 = S4XC6H8-15E2M 1.23E+35 -7.76 9930.0 ! Ref to C2H4+C2H3 = C4H7
PLOG / 0.039 6.15E+34 -7.76 9930.0 /
PLOG / 0.1 1.23E+35 -7.76 9930.0 /
PLOG / 1.0 7.93E+38 -8.47 14220.0/
PLOG / 10 2.99E+36 -7.40 15480.0/
P1XCH2C6H9-15E=aC3H4+C4H7 1.00E+12 0.0 51000 ! Ref to iC4H7=aC3H4+CH3
PLOG / 0.039 1.00E+12 0.0 51000/ ! EST /10
PLOG / 1.0 1.00E+13 0.0 51000/ ! 2009 Yasunaga et al.
! cC7H12 reactions
MCH-1E+H = S3XMCH-1E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571
MCH-1E+CH3= S3XMCH-1E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
S3XMCH-1E+H(+M)=MCH-1E(+M) 1.33E+14 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *2/3
LOW/ 0.89E+60 -12.00 5967.8 /
TROE /0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S2XMCH-5E+H(+M)=MCH-1E(+M) 1.33E+14 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *2/3
LOW/ 0.89E+60 -12.00 5967.8 /
TROE /0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
MCH-1E+H = S2XMCH-5E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571
MCH-1E+CH3= S2XMCH-5E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
CH2S2XcC6H9+H(+M)=MCH-1E(+M) 2.00E+14 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M)
LOW /1.33E+60 -12.00 5967.8/
TROE /0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/

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MCH-1E+H = CH2S2XcC6H9+H2 1.73E5 2.5 2492 ! allylp LLNL-MI-407571
MCH-1E+CH3= CH2S2XcC6H9+CH4 2.2098 3.5 5675 ! allylp LLNL-MI-407571
MCH-2E+H = S2XMCH-3E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571
MCH-2E+CH3= S2XMCH-3E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
S2XMCH-3E+H(+M)=MCH-2E(+M) 1.33E+14 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *2/3
LOW/ 0.89E+60 -12.00 5967.8 /
TROE /0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
MCH-2E+H = T1XMCH-2E+H2 2.65E6 2.2 0.0 ! allylt LLNL-MI-407571
MCH-2E+CH3= T1XMCH-2E+CH4 4.613 3.1 2330 ! allylt LLNL-MI-407571
T1XMCH-2E+H(+M)=MCH-2E(+M) 0.67E+14 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *1/3
LOW / 0.44E+60 -12.00 5967.8/
TROE / 0.020 1096.6 1096.6 6859.5/
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S3XcC6H9-1E+CH3(+M)=MCH-2E(+M) 1.00E+14 -0.32 -262. ! Ref to aC3H5+CH3(+M)=
1(+M)
LOW / 3.51E+60 -12.97 6000./
TROE / 0.896 60000 1606 6118/
H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/
MCH-3E+H = S2XMCH-3E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571
MCH-3E+CH3= S2XMCH-3E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
S2XMCH-3E+H(+M)=MCH-3E(+M) 1.33E+14 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *2/3
LOW / 0.89E+60 -12.00 5967.8 /
TROE / 0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
MCH-3E+H = S5XMCH-3E+H2 3.376E05 2.36 207 ! allyls LLNL-MI-407571
MCH-3E+CH3= S5XMCH-3E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
S5XMCH-3E+H(+M)=MCH-3E(+M) 1.33E+14 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *2/3
LOW / 0.89E+60 -12.00 5967.8 /
TROE/ 0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
CH2cC6H10+H = CH2S2XcC6H9+H2 6.752E05 2.36 207 ! (ax4) allyls LLNL-MI-407571
CH2cC6H10+CH3= CH2S2XcC6H9+CH4 7.38 3.31 4002 ! (ax4) allyls LLNL-MI-407571
```

```
CH2S2XcC6H9+H(+M)=CH2cC6H10(+M) 4.0E+14 0.00 0.0 ! Ref to aC3H5+H(+M) = C3H6(+M) *2
LOW / 2.66E+60 -12.00 5967.8 /
TROE/ 0.020 1096.6 1096.6 6859.5 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
CH2cC6H10+H=¿C2H4+P1XCH2C4H5-13E+H2 1.08E+5 2.5 -1900 ! 2010 Pousse et al.
CH2cC6H10+CH3=¿C2H4+P1XCH2C4H5-13E+CH4 2E+11 0 7300 ! 2010 Pousse et al.
MCH-1E=C4H5-13E2M+C2H4 5.0E+78 -18.94 98386 ! Ref to cC6H10 = C4H6+C2H4
PLOG / 0.039 5.0E+78 -18.94 98386 /
PLOG / 0.197 2.60E+70 -16.36 95510 /
PLOG / 1.0 3.81E+25 -3.58 64034 /
PLOG / 1.0E+5 8.31E+13 0.387 64116 /
MCH-2E=C5H8-13E+C2H4 5.0E+78 -18.94 98386 ! Ref to cC6H10 = C4H6+C2H4
PLOG / 0.039 5.0E+78 -18.94 98386 /
PLOG / 0.197 2.60E+70 -16.36 95510 /
PLOG / 1.0 3.81E+25 -3.58 64034 /
PLOG / 1.0E+5 8.31E+13 0.387 64116 /
MCH-3E=C4H6+C3H6 5.0E+78 -18.94 98386 ! Ref to cC6H10 = C4H6+C2H4
PLOG / 0.039 5.0E+78 -18.94 98386 /
PLOG / 0.197 2.60E+70 -16.36 95510 /
PLOG / 1.0 3.81E+25 -3.58 64034 /
PLOG / 1.0E+5 8.31E+13 0.387 64116 /
CH2cC6H10=C6H9-15E2M 1.33E+137 -34.70 162775 ! Ref to cC6H12
PLOG / 0.039 1.33E+137 -34.70 162775/ !
PLOG / 0.066 5.96E+139 -35.26 166598/ !
PLOG / 0.263 1.82E+143 -35.99 172904/ !
PLOG / 1.0E+5 8.76E+17 0.00 91940 / !
! C7H12 dienes reactions
C7H12-13E+H = C5H10-1E+C2H3 1.46E+30 -4.34 21647.0 ! =(C4H6+H)
C7H12-13E= C2H5+lC5H7 1.07E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7
PLOG / 0.039 1.07E+80 -19.33 95177/
PLOG / 0.066 2.50E+68 -16.040 86832/
PLOG / 0.132 1.480E+59 -13.261 82596/
PLOG / 0.197 2.43E+61 -13.999 82637/
PLOG / 0.263 3.75E+59 -13.427 82179/
PLOG / 1.0E+5 1.46E+16 0.00 69120/
```

C7H12-13E=aC3H5+C4H7 2.14E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7 *2

PLOG / 0.039 2.14E+80 -19.33 95177/

PLOG / 0.066 5.00E+68 -16.040 86832/

PLOG / 0.132 2.96E+59 -13.261 82596/

PLOG / 0.197 4.86E+61 -13.999 82637/

PLOG / 0.263 7.50E+59 -13.427 82179/

PLOG / 1.0E+5 2.92E+16 0.00 69120/

C7H12-13E+H = S3XC7H11-16E+H2 6.752E+5 2.36 207 ! (ax4) allyls LLNL-MI-407571

C7H12-13E+CH3 = S3XC7H11-16E+CH4 7.38 3.31 4002 ! (ax4) allyls LLNL-MI-407571

C7H12-15E= aC3H5+SAXC4H7 1.07E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

C7H12-15E+H = S3XC7H11-15E+H2 3.376E5 2.36 207 ! allyls LLNL-MI-407571

C7H12-15E+H = S4XC7H11-15E+H2 3.376E5 2.36 207 ! allyls LLNL-MI-407571

C7H12-15E+CH3 = S3XC7H11-15E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C7H12-15E+CH3 = S4XC7H11-15E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C7H12-15E+H = P7XC7H11-15E+H2 1.7298E5 2.5 2492 ! allylP LLNL-MI-407571

C7H12-15E+CH3 = P7XC7H11-15E+CH4 2.2098 3.5 5675 ! allylP LLNL-MI-407571

C6H9-15E3M = aC3H5+SAXC4H7 1.07E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

C6H9-15E3M = S3XC6H9-15E+CH3 1.07E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

C6H9-15E3M+H = S4XC6H8-15E3M+H2 3.376E5 2.36 207 ! allyls LLNL-MI-407571

C6H9-15E3M+CH3 = S4XC6H8-15E3M+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C6H9-15E3M+H = P1XCH2-3C6H9-15E+H2 6.651E05 2.54 6756 ! primary LLNL-MI-407571

C6H9-15E3M+CH3 = P1XCH2-3C6H9-15E+CH4 4.521E-1 3.65 7154 ! primary LLNL-MI-407571

C6H9-15E3M+H = T1XC6H8-15E3M+H2 2.65E6 2.2 0.0 ! allylt LLNL-MI-407571

C6H9-15E3M+CH3 = T1XC6H8-15E3M+CH4 4.613 3.1 2330 ! allylt LLNL-MI-407571

C7H12-24E = S2XC6H9-13E+CH3 1.07E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

CH2-3-C6H10-E = P1XCH2C4H5-13E+C2H5 1.07E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

CH2-3-C6H10-E+H = C5H10-1E+C2H3 1.46E+30 -4.34 21647.0 ! =(C4H6+H)

CH2-3-C6H10-E+H = C4H6+nC3H7 8.80E+16 -1.05 6461.0 ! Ref to C3H6+H = C2H4+CH3

CH2-3-C6H10-E+H = C4H5-13E2M+C2H5 3.20E+22 -2.39 11180 ! Ref to C4H8-1+H = C3H6+CH3

C6H9-15E2M+H = S3XC6H8-15E2M+H2 3.376E5 2.36 207 ! allyls LLNL-MI-407571

C6H9-15E2M+H = S4XC6H8-15E2M+H2 3.376E5 2.36 207 ! allyls LLNL-MI-407571

C6H9-15E2M+H = P1XCH2C6H9-15E+H2 1.7298E5 2.5 2492 ! allylp LLNL-MI-407571

C6H9-15E2M+CH3 = S3XC6H8-15E2M+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C6H9-15E2M+CH3 = S4XC6H8-15E2M+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C6H9-15E2M+CH3 = P1XCH2C6H9-15E+CH4 2.2098 3.5 5675 ! allylp LLNL-MI-407571

C6H9-15E2M = aC3H5+iC4H7 1.07E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

C6H9-13E5M = S2XC6H9-13E+CH3 2.14E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7 *2

PLOG / 0.039 2.14E+80 -19.33 95177/

PLOG / 0.066 5.00E+68 -16.040 86832/

PLOG / 0.132 2.96E+59 -13.261 82596/

PLOG / 0.197 4.86E+61 -13.999 82637/

PLOG / 0.263 7.50E+59 -13.427 82179/

PLOG / 1.0E+5 2.92E+16 0.00 69120/

! C7H13 alkenyl reactions

P7XC7H13-1E (+M) = C2H4+P5XC5H9-1E (+M) 3.98E+12 0.12 27571.6 ! Ref to P1XC6H11-1E(+M) = C4H7+C2H4(+M)

LOW / 3.30E-43 18.35 -602.5/

TROE / -13.87 227 28 50000.0/

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C7H12-13E+H(+M) = P7XC7H13-1E(+M) 1.33E+13 0.00 3260.7 ! Ref to C3H6+H(+M) = nC3H7(+M)

LOW / 6.26E+38 -6.66 7000.0/

TROE / 1.000 1000.0 1310.0 48097.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

P7XC7H13-1E(+M) = S3XC7H13-1E(+M) 1.55E+02 2.83 15566.2 ! Ref to P1XC6H11-1E(+M) = S3XC6H11-1E(+M)

LOW / 1.50E-30 14.56 -602.4/

TROE / -13.59 214 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S6XC7H13-1E(+M) = C4H7+C3H6(+M) 5.50E+11 0.55 28084.3 ! 08TSAb JetSurF 2.0

LOW/ 3.10E-43 18.418 -602.9 /

TROE/ -32.13 207.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S6XC7H13-1E(+M) = S3XC7H13-1E(+M) 1.55E+02 2.83 15566.2 ! 08/TSwip JetSurF 2.0

LOW/ 1.50E-30 14.56 -602.4 /

TROE/ -13.59 214 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C7H12-13E+H(+M) = S6XC7H13-1E(+M) 1.33E+13 0.00 1559.8 ! Ref to C4H8-1+H(+M) = sC4H9(+M)

LOW / 8.70E+42 -7.50 4721.8/

TROE / 1.000 1000.0 645.4 6844.3 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C7H12-15E+H(+M) = S6XC7H13-1E(+M) 1.33E+13 0.00 1559.8 ! Ref to C4H8-2+H(+M) = sC4H9(+M)

LOW / 8.70E+42 -7.50 4721.8 /

TROE / 1.000 1000.0 645.4 6844.3 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S3XC7H13-1E(+M) = C4H6+nC3H7(+M) 3.39E+11 0.66 32262.9 ! 08/TSAwip JetSurF 2.0

LOW/ 4.00E-42 18.045 -602.6 /

TROE/ -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S3XC7H13-1E(+M) = C7H12-13E+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7 = C4H6 + H *2/3

LOW / 3.07E-37 15.37 -603.1/

TROE / -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

P6XC6H10-1E4M(+M) = S4XC5H9-1E+C2H4(+M) 1.76E+11 0.57 28791.0 ! 08TSAa JetSurF 2.0

LOW/ 2.80E-44 18.729 -602.5 /

TROE / -14.66 219.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C6H9-15E3M+H(+M) = P6XC6H10-1E4M(+M) 1.33E+13 0.00 3260.7 ! Ref to C3H6+H(+M) = nC3H7(+M)

LOW / 6.26E+38 -6.66 7000.0/

TROE / 1.000 1000.0 1310.0 48097.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

P6XC6H10-1E4M(+M) = S3XC6H10-1E4M(+M) 1.55E+02 2.83 15566.2 ! 08/TSwip JetSurF 2.0

LOW/ 1.50E-30 14.56 -602.4 /

TROE/ -13.59 214 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S3XC6H10-1E4M(+M) = C5H8-13E+C2H5(+M) 3.39E+11 0.66 31262.9 ! 08/TSAwip (-1 kcal/mol Ctert-Csec) JetSurF 2.0

LOW / 4.00E-42 18.045 -602.6/

TROE / -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S3XC6H10-1E4M(+M) = C6H10-13E+CH3(+M) 3.39E+11 0.66 31262.9 ! Ref to S3XC6H11-1E(+M) = C4H6+C2H5(+M)

LOW / 4.00E-42 18.045 -602.6/

TROE / -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

P7XC7H13-2E(+M) = S3XC5H9-1E+C2H4(+M) 9.12E+11 0.31 27237.8 ! 08TSAb (lumped C5H9) JetSurF 2.0

LOW / 1.80E-57 23.463 -602.4 /

TROE/ -2.46 206.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C7H12-15E+H(+M) = P7XC7H13-2E(+M) 1.33E+13 0.00 3260.7 ! Ref to C3H6+H(+M) = nC3H7(+M)

LOW / 6.26E+38 -6.66 7000.0/

TROE / 1.000 1000.0 1310.0 48097.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

P7XC7H13-2E(+M) = S4XC7H13-2E(+M) 1.55E+02 2.83 15566.2 ! 08/TSwip JetSurF 2.0

LOW / 1.50E-30 14.56 -602.4 /

TROE / -13.59 214 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S4XC7H13-2E(+M) = C5H8-13E+C2H5(+M) 3.39E+11 0.66 32262.9 ! Ref to S3XC6H11-1E(+M) = C4H6+C2H5(+M)

LOW / 4.00E-42 18.05 -602.6 /

TROE/ -18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

S4XC7H13-2E(+M) = C7H12-24E+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7 = C4H6 + H *2/3

LOW / 3.07E-37 15.37 -603.1/

TROE/ -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

S4XC7H13-2E(+M) = C7H12-13E+H(+M) 4.70E+08 1.32 44697.6 ! Ref to SAXC4H7 = C4H6 + H

LOW / 4.60E-37 15.37 -603.1/

TROE/ -51.87 258 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/

P6XC6H10-1E3M(+M) = P4XC4H6-1E3M+C2H4(+M) 2.38E+11 0.51 27281.5 ! 08TSAb JetSurF 2.0

LOW / 1.80E-57 23.463 -602.4 /

TROE / -2.46 206.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C6H9-15E3M+H(+M) = P6XC6H10-1E3M(+M) 1.33E+13 0.00 3260.7 ! Ref to C3H6+H(+M) = nC3H7(+M)

LOW / 6.26E+38 -6.66 7000.0/

TROE / 1.000 1000.0 1310.0 48097.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

P6XC6H10-1E3M(+M) = T3XC6H10-1E3M(+M) 8.60E+01 2.62 8722.9 ! 08TSAc & Est-2 JetSurF 2.0

LOW / 8.10E-33 15.214 -677.4/

TROE / -30.39 206.0 28.0 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

T3XC6H10-1E3M(+M) = C4H5-13E2M+C2H5(+M) 3.39E+11 0.66 32262.9 ! Ref to S3XC6H11-1E(+M) = C4H6+C2H5(+M)

LOW / 4.00E-42 18.05 -602.6 /

TROE /-18.50 246 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

P1XCH2C6H11-1E(+M) = C4H7+C3H6(+M) 1.76E+11 0.57 28791.6 ! 08TSAc (2-methyl-pent-4-yl) JetSurF 2.0

LOW / 4.70E-39 16.77 -603.1/

TROE /-27.89 216 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

P1XCH2C6H11-1E(+M) = C6H10-15E+CH3(+M) 1.76E+11 0.57 28791.6 ! 08TSAc (2-methyl-pent-4-yl) JetSurF 2.0

LOW / 4.70E-39 16.77 -603.1/

TROE/ -27.89 216 28 50000.0 /

H2/2/ CH4/2/ C2H6/3/ AR/0.7/

C6H9-15E2M+H(+M) = P1XCH2C6H11-1E(+M) 1.33E+13 0.00 3260.7 ! Ref to iC4H8+H(+M) = iC4H9(+M)
LOW / 6.26E+38 -6.66 7000.0 /
TROE / 1.000 1000 1310.0 48097.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
P1XCH2C6H11-1E(+M) = S3XC6H10-1E5M(+M) 1.55E+02 2.83 15566.2 ! 08/TSwip JetSurF 2.0
LOW / 1.50E-30 14.56 -602.4 /
TROE/ -13.59 214 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S3XC6H10-1E5M(+M) = C4H6+iC3H7(+M) 3.39E+11 0.66 31262.9 ! 08/TSAwip (-1 kcal/mol Ctert-Csec) JetSurF 2.0
LOW / 4.00E-42 18.045 -602.6/
TROE /-18.50 246 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S3XC6H10-1E5M(+M) = C6H9-13E5M+H(+M) 3.13E+08 1.32 44697.6 ! Ref to SAXC4H7 = C4H6 + H *2/3
LOW / 3.07E-37 15.37 -603.1/
TROE /-51.87 258 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/
P6XC6H10-1E2M(+M) = P4XC4H6-1E2M+C2H4(+M) 3.98E+12 0.12 27571.6 ! 08/TSAwip JetSurF 2.0
LOW / 3.30E-43 18.35 -602.5 /
TROE /-13.87 227 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
C6H9-15E2M+H(+M) = P6XC6H10-1E2M(+M) 1.33E+13 0.00 3260.7 ! Ref to C3H6+H(+M) = nC3H7(+M)
LOW / 6.26E+38 -6.66 7000.0/
TROE / 1.000 1000.0 1310.0 48097.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
P6XC6H10-1E2M(+M) = S3XC6H10-1E2M(+M) 1.55E+02 2.83 15566.2 ! 08/TSwip JetSurF 2.0
LOW / 1.50E-30 14.56 -602.4 /
TROE /-13.59 214 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/
S3XC6H10-1E2M(+M) = C4H5-13E2M+C2H5(+M) 3.39E+11 0.66 32262.9 ! Ref to S3XC6H11-1E(+M) = C4H6+C2H5(+M)
LOW / 4.00E-42 18.05 -602.6 /
TROE / -18.50 246 28 50000.0 /
H2/2/ CH4/2/ C2H6/3/ AR/0.7/

```
! methylcyclohexane reactions
! H-abstractions of methylcyclohexane
MCH+H = PXCH2cC6H11+H2 6.66E+06 2.13 8894.8
MCH+H = T1XMCH+H2 4.53E+06 2.11 4098.6
MCH+H = S2XMCH+H2 2.08E+07 2.10 6474.4
MCH+H = S3XMCH+H2 2.07E+07 2.12 6441.2
MCH+H = S4XMCH+H2 1.16E+07 2.11 6339.1
MCH+CH3 = PXCH2cC6H11+CH4 3.75E+01 3.27 13516.0 ! 10LV JetSurF 2.0
MCH+CH3 = T1XMCH+CH4 1.91E+01 3.27 9022.0 ! 10LV JetSurF 2.0
MCH+CH3 = S2XMCH+CH4 6.68E+01 3.21 11418.0 ! 10LV JetSurF 2.0
MCH+CH3 = S3XMCH+CH4 7.18E+01 3.26 11303.0 ! 10LV JetSurF 2.0
MCH+CH3 = S4XMCH+CH4 1.82E+01 3.36 10931.0 ! 10LV JetSurF 2.0
! isomerization and decomposition of methylcyclohexane
MCH = cC6H11+CH3 1.00 0.00 0.00 ! 2013 Zhang et al.
PLOG / 0.01 1.85E+105 -26.15 129214 /
PLOG / 0.0395 1.19E+92 -22.23 122595 /
PLOG / 0.197 1.50E+80 -18.67 116938 /
PLOG / 0.395 8.65E+63 -13.89 108211 /
PLOG / 1 5.93E+64 -14.15 108486 /
PLOG / 10 3.59E+45 -8.56 97430 /
PLOG / 100 1.66E+33 -4.99 90100 /
PLOG / 1.0E+5 1.10E+27 -3.20 86385 /
MCH = C7H14-1E 1.00 0.00 0.00 ! 2013 Zhang et al.
PLOG / 0.01 5.49E+115 -29.26 143180 /
PLOG / 0.0395 1.03E+104 -25.68 138280 /
PLOG / 0.197 1.92E+88 -20.96 130954 /
PLOG / 0.395 3.07E+80 -18.65 126930 /
PLOG / 1 5.57E+69 -15.49 121178 /
PLOG / 10 4.90E+44 -8.17 107073 /
PLOG / 100 7.98E+26 -3.02 96627 /
PLOG / 1.0E+5 1.09E+17 -0.16 90732 /
MCH = C7H14-2E 1.00 0.00 0.00 ! 2013 Zhang et al.
PLOG / 0.01 9.52E+114 -28.98 140737 /
PLOG / 0.0395 1.74E+103 -25.40 135829 /
PLOG / 0.197 3.34E+87 -20.68 128511 /
PLOG / 0.395 5.32E+79 -18.37 124487 /
PLOG / 1 9.66E+68 -15.21 118735 /
PLOG / 10 8.51E+43 -7.89 104630 /
PLOG / 100 1.38E+26 -2.74 94184 /
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PLOG / 1.0E+5 1.90E+16 0.12 88289 /
MCH = C6H11-1E2M 1.00 0.00 0.00 ! 2013 Zhang et al.
PLOG / 0.01 2.25E+132 -34.10 155250 /
PLOG / 0.0395 1.46E+109 -27.20 144350 /
PLOG / 0.197 4.09E+93 -22.49 137505 /
PLOG / 0.395 4.87E+85 -20.13 133555 /
PLOG / 1 3.27E+74 -16.83 127710 /
PLOG / 10 3.09E+47 -8.92 112705 /
PLOG / 100 2.18E+27 -3.08 100948 /
PLOG / 1.0E+5 6.04E+15 0.27 94051 /
MCH = C6H11-1E5M 1.00 0.00 0.00 ! 2013 Zhang et al.
PLOG / 0.01 1.99E+132 -34.11 154207 /
PLOG / 0.0395 1.28E+109 -27.20 143306 /
PLOG / 0.197 3.61E+93 -22.49 136462 /
PLOG / 0.395 4.30E+85 -20.13 132511 /
PLOG / 1 2.89E+74 -16.83 126667 /
PLOG / 10 2.73E+47 -8.93 111662 /
PLOG / 100 1.93E+27 -3.08 99905 /
PLOG / 1.0E+5 5.34E+15 0.27 93008 /
MCH = C6H11-1E3M 1.00 0.00 0.00 ! 2013 Zhang et al.
PLOG / 0.01 1.70E+119 -30.34 147025 /
PLOG / 0.0395 1.77E+108 -26.94 142902 /
PLOG / 0.197 4.67E+92 -22.23 136004 /
PLOG / 0.395 4.07E+107 -26.52 143245 /
PLOG / 1 3.71E+73 -16.58 126164 /
PLOG / 10 5.09E+46 -8.72 111220 /
PLOG / 100 6.68E+26 -2.95 99619 /
PLOG / 1.0E+5 2.53E+15 0.36 92802 /
MCH = C6H11-1E4M 1.00 0.00 0.00 ! 2013 Zhang et al.
PLOG / 0.01 1.87E+119 -30.34 146825 /
PLOG / 0.0395 1.95E+108 -26.95 142703 /
PLOG / 0.197 5.13E+92 -22.24 135803 /
PLOG / 0.395 4.47E+107 -26.52 143045 /
PLOG / 1 4.07E+73 -16.58 125964 /
PLOG / 10 5.59E+46 -8.72 111019 /
PLOG / 100 7.33E+26 -2.95 99418 /
PLOG / 1.0E+5 2.78E+15 0.35 92602 /
! C7H14 alkenes reactions
C7H14-1E = pC4H9+aC3H5 1.07E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7
PLOG / 0.039 1.07E+80 -19.33 95177/
```

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PLOG / 0.066 2.50E+68 -16.040 86832/
PLOG / 0.132 1.480E+59 -13.261 82596/
PLOG / 0.197 2.43E+61 -13.999 82637/
PLOG / 0.263 3.75E+59 -13.427 82179/
PLOG / 1.0E+5 1.46E+16 0.00 69120/
C7H14-1E = C4H8-1+C3H6 7.08E+06 1.65 53752.0 !
PLOG / 0.039 3.54E+05 1.65 53752.0/ ! /20 EST
PLOG / 1.0 7.08E+06 1.65 53752.0/ ! JetSurF 2.0
C7H14-1E+H = S3XC7H13-1E+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571
C7H14-1E+CH3 = S3XC7H13-1E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
C7H14-2E = SAXC4H7+nC3H7 1.07E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7
PLOG / 0.039 1.07E+80 -19.33 95177 /
PLOG / 0.066 2.50E+68 -16.040 86832 /
PLOG / 0.132 1.480E+59 -13.261 82596 /
PLOG / 0.197 2.43E+61 -13.999 82637 /
PLOG / 0.263 3.75E+59 -13.427 82179 /
PLOG / 1.0E+5 1.46E+16 0.00 69120 /
C7H14-2E = C4H8-1+C3H6 1.42E+07 1.65 53752.0 !
PLOG / 0.039 7.0E+05 1.65 53752.0/ ! /20 EST
PLOG / 1.0 1.42E+07 1.65 53752.0/ ! JetSurF 2.0
C7H14-2E+H = S3XC7H13-1E+H2 1.73E5 2.5 2492 ! allylp LLNL-MI-407571
C7H14-2E+CH3 = S3XC7H13-1E+CH4 2.2098 3.5 5675 ! allylp LLNL-MI-407571
C7H14-2E+H = S4XC7H13-2E+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571
C7H14-2E+CH3 = S4XC7H13-2E+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571
C6H11-1E2M = iC4H7+nC3H7 1.07E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7
PLOG / 0.039 1.07E+80 -19.33 95177/
PLOG / 0.066 2.50E+68 -16.040 86832/
PLOG / 0.132 1.480E+59 -13.261 82596/
PLOG / 0.197 2.43E+61 -13.999 82637/
PLOG / 0.263 3.75E+59 -13.427 82179/
PLOG / 1.0E+5 1.46E+16 0.00 69120/
C6H11-1E2M = iC4H8+C3H6 7.08E+06 1.65 53752.0 ! EST, ref to C7H14-1E
PLOG / 0.039 3.54E+05 1.65 53752.0/ !
PLOG / 1.0 7.08E+06 1.65 53752.0/ !
```

C6H11-1E2M+H = S3XC6H10-1E2M+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C6H11-1E2M+CH3 = S3XC6H10-1E2M+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C6H11-1E5M = aC3H5+iC4H9 1.07E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

C6H11-1E5M+H = S3XC6H10-1E5M+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C6H11-1E5M+CH3 = S3XC6H10-1E5M+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C6H11-1E4M = aC3H5+sC4H9 1.07E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7

1.07E+80 -19.33 95177 !

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

C6H11-1E4M = C3H6+C4H8-2 7.08E+06 1.65 53752.0 ! EST, ref to C7H14-1E

PLOG / 0.039 3.54E+05 1.65 53752.0/ !

PLOG / 1.0 7.08E+06 1.65 53752.0/ !

C6H11-1E4M+H = S3XC6H10-1E4M+H2 3.376E+5 2.36 207 ! allyls LLNL-MI-407571

C6H11-1E4M+CH3 = S3XC6H10-1E4M+CH4 3.69 3.31 4002 ! allyls LLNL-MI-407571

C6H11-1E3M = SAXC4H7+nC3H7 1.07E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

PLOG / 0.197 2.43E+61 -13.999 82637/

PLOG / 0.263 3.75E+59 -13.427 82179/

PLOG / 1.0E+5 1.46E+16 0.00 69120/

C6H11-1E3M = S3XC6H11-1E+CH3 1.07E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7

```
PLOG / 0.039 1.07E+80 -19.33 95177/
PLOG / 0.066 2.50E+68 -16.040 86832/
PLOG / 0.132 1.480E+59 -13.261 82596/
PLOG / 0.197 2.43E+61 -13.999 82637/
PLOG / 0.263 3.75E+59 -13.427 82179/
PLOG / 1.0E+5 1.46E+16 0.00 69120/
C6H11-1E3M = C4H8-2+C3H6 7.08E+06 1.65 53752.0 ! EST, ref to C7H14-1E
PLOG / 0.039 3.54E+05 1.65 53752.0/ !
PLOG / 1.0 7.08E+06 1.65 53752.0/ !
C6H11-1E3M+H = T3XC6H10-1E3M+H2 2.65E+6 2.2 0.0 ! allylt LLNL-MI-407571
C6H11-1E3M+CH3 = T3XC6H10-1E3M+CH4 4.613 3.1 2330 ! allylt LLNL-MI-407571
! aromatic reactions (needed)
! reactions of C6H4 C6H3 C6H2
o-C6H4=C4H2+C2H2 6.50E+14 0.0 83000.0 !
PLOG / 0.039 6.50E+13 0.0 83000.0/ ! /10 for falloff effect
PLOG / 1.0 6.50E+14 0.0 83000.0 / ! 2007 Xu et al.
nC4H3+C2H2=o-C6H4+H 9.20E+33 -6.57 15900. ! 1997 Wang&Frenklach
PLOG / 0.013 9.20E+33 -6.57 15900./ ! 10 Torr RRKM
PLOG / 0.026 1.90E+36 -7.21 17900./ ! 20 Torr RRKM
PLOG / 0.118 3.50E+41 -8.63 23000./ ! 90 Torr RRKM
PLOG / 1 6.90E+46 -10.01 30100./ ! 760 Torr RRKM
PLOG / 10 3.10E+49 -10.59 37700./ ! 7600 Torr RRKM
l-C6H4+H=o-C6H4+H 8.70E+45 -9.61 22300. ! 1997 Wang&Frenklach
PLOG / 0.013 8.70E+45 -9.61 22300./ ! 10 Torr RRKM
PLOG / 0.026 2.20E+47 -9.98 24000. / ! 20 Torr RRKM
PLOG / 0.118 9.70E+48 -10.37 27000. / ! 90 Torr RRKM
PLOG / 1 1.40E+54 -11.70 34500. / ! 760 Torr RRKM
PLOG / 10 5.70E+55 -11.98 41900. / ! 7600 Torr RRKM
l-C6H4+H=C6H3+H2 1.33E+06 2.5 9240.0 ! USC Mech V2.0
C3H2+C3H2=l-C6H4 3.00E+11 0.0 0.0 ! Est. ref: 1987 Wu&Kern C3H3+C3H3=A1
C4H2+C2H2=l-C6H4 4.47E+11 0.0 30010.0 ! Est. Ref to C4H4+C2H2=A1
nC4H3+C2H2=l-C6H4+H 3.70E+16 -1.2 11100.0 ! 1997 Wang&Frenklach
PLOG / 0.013 1.40E+15 -0.81 10000./ ! 10 Torr RRKM
PLOG / 0.026 3.70E+16 -1.21 11100./ ! 20 Torr RRKM
PLOG / 0.118 1.80E+19 -1.95 13200./ ! 90 Torr RRKM
PLOG / 1 2.50E+14 -0.56 10600./ ! 760 Torr RRKM
PLOG / 10 1.20E+17 -1.28 13700./ ! 7600 Torr RRKM
C4H4+C2H=l-C6H4+H 1.20E+13 0.0 0.0 ! USC Mech V2.0
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C6H3+H=l-C6H4 4.20E+44 -10.3 7890.0 ! 1997 Wang&Frenklach 0.026 atm RRKM
C5H3+CH2=l-C6H4+H 5.00E+13 0.0 0.0 ! ABF
C4H2+C2H = C6H2+H 9.60E+13 0.0 0. ! = C2H2 + C2H JetSurF 2.0
C4H2+C2H=C6H3 1.10E+30 -6.30 2790.0 ! 1997 Wang&Frenklach
PLOG / 0.026 1.10E+30 -6.30 2790.0/ ! 20 Torr RRKM
PLOG / 0.118 1.30E+30 -6.12 2510.0/ ! 90 Torr RRKM
PLOG / 1 4.50E+37 -7.68 7100.0/ ! 760 Torr RRKM
C6H2+H=C6H3 4.30E+45 -10.2 13250.0 ! 1997 Wang&Frenklach
PLOG / 0.026 4.30E+45 -10.15 13250.0/ ! 20 Torr RRKM
PLOG / 0.118 2.60E+46 -10.15 15500.0/ ! 90 Torr RRKM
PLOG / 1 1.10E+30 -4.92 10800.0/ ! 760 Torr RRKM
C6H3+H=C4H2+C2H2 2.40E+19 -1.6 2800.0 ! 1997 Wang&Frenklach
PLOG / 0.026 2.40E+19 -1.60 2800.0/ ! 20 Torr RRKM
PLOG / 0.118 3.70E+22 -2.50 5140.0/ ! 90 Torr RRKM
PLOG / 1 2.80E+23 -2.55 10780.0/ ! 760 Torr RRKM
! reactions of A1-
A1-=o-C6H4+H 3.00E+13 0.0 72923.0 ! 2005 Baulch et al.
nC4H3+C2H2=A1- 1.40E+67 -17.42 23000. ! 1997 Wang&Frenklach
PLOG / 0.013 1.40E+67 -17.42 23000./ ! 10 Torr RRKM
PLOG / 0.026 2.30E+68 -17.65 24400./ ! 20 Torr RRKM
PLOG / 0.118 9.80E+68 -17.58 26500./ ! 90 Torr RRKM
PLOG / 1 9.60E+70 -17.77 31300./ ! 760 Torr RRKM
PLOG / 10 1.90E+63 -15.25 30600./ ! 7600 Torr RRKM
! A1-+H=o-C6H4+H2 4.40E-13 7.831 9261.0 ! MIT [2001 Mebel et al. 100 torr]
nC6H5=A1- 1.66E+11 0.0 16350.0 ! MIT [1987 Dewar et al.]
l-C6H4+H=A1- 4.40E+74 -19.09 25800. ! 1997 Wang&Frenklach
PLOG / 0.013 4.40E+74 -19.09 25800./ ! 10 Torr RRKM
PLOG / 0.026 3.60E+77 -20.09 28100./ ! 20 Torr RRKM
PLOG / 0.118 4.70E+78 -20.10 29500./ ! 90 Torr RRKM
PLOG / 1 1.70E+78 -19.72 31400./ ! 760 Torr RRKM
PLOG / 10 3.90E+69 -16.63 34100./ ! 7600 Torr RRKM
C3H3+C3H3=A1-+H 2.02E+33 -6.0 15940.0 ! 2009 Hansen et al C3H4 FLAME
A1-+H=o-C6H4+H2 2.36E-06 5.80 11714 !2001 A. M. Mebel and M.C.Lin
PLOG/ 0.132 2.36E-06 5.80 11714/
PLOG/ 1.000 1.16E-14 8.13 8766/
PLOG/ 10.00 2.58E-22 10.22 5350/
! reactions of A1
fulvene=A1 5.6234E+81 -19.36 121500. ! J. A. Miller Mechanism
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PLOG /0.03947 5.6234E+81 -19.36 121500./
PLOG /1. 1.4454E+45 -8.900 96999./
PLOG /10. 2.9512E+31 -4.970 88465./
fulvene=A1-+H 2.5704E+97 -23.16 153470. ! J. A. Miller Mechanism
PLOG /0.03947 2.5704E+97 -23.16 153470./
PLOG /1. 2.2387E+68 -14.65 142570./
PLOG /10. 8.5114E+24 -2.505 113330./
A1=A1-+H 1.3490E+108 -25.81 181750. ! J. A. Miller Mechanism
PLOG /0.03947 1.3490E+108 -25.81 181750./
PLOG /1. 6.3096E+60 -12.40 148070./
PLOG /10. 5.4954E+38 -6.178 132000./
C3H3+C3H3=fulvene 7.25E+65 -16.0 25035.0 !
PLOG /0.03947 7.25E+65 -16.0 25035.0/ ! 2009 Hansen et al C3H4 FLAME
PLOG /1. 1.3798E+66 -15.66 28260./ ! J. A. Miller Mechanism
PLOG /10. 1.2584E+56 -12.61 23515./ ! J. A. Miller Mechanism
C3H3+C3H3=A1 1.64E+66 -15.9 27529.0 !
PLOG /0.03947 1.64E+66 -15.9 27529.0/ ! 2009 Hansen et al C3H4 FLAME
PLOG /1. 3.1609E+55 -12.55 22264./ ! J. A. Miller Mechanism
PLOG /10. 3.8888E+50 -11.01 20320./ ! J. A. Miller Mechanism
aC3H4+C3H2=A1 7.40E+12 -0.7 920.0 ! 2002 D'Anna & Kent
pC3H4+C3H2=A1 1.40E+13 -0.8 1030.0 ! 2002 D'Anna & Kent
A1+H=A1-+H2 1.420E+08 1.77 13056.0 ! 2004 Violi et al.
A1-+CH4=A1+CH3 3.89E-03 4.6 5256.0 ! 1999 Tokmakov et al.
A1-+C2H6=A1+C2H5 2.10E+11 0.0 4443.0 ! 2001 Park et al.
C5H6+A1-=C5H5+A1 3.10E+11 0.0 5500.0 ! 2001 Mac&Bac
nC4H3+C2H3=A1 2.87E+14 0.0 817.0 ! 2006 Richter et al.
aC3H4+C3H3=A1+H 2.20E+11 0.0 2000.0 ! 2002 D'Anna & Kent
C4H4+C2H3=A1+H 1.90E+12 0.0 2510.0 ! 1997 Lindstedt&Skevis
pC3H4+C3H3=A1+H 2.20E+11 0.0 2000.0 ! MIT 1987 Wu&Kern
C4H4+C2H2=A1 4.47E+11 0.0 30010.0 ! MIT 1986 Chanmugathas&Heicklen
nC4H5+C2H3=A1+H2 1.84E-13 7.1 -3611.0 ! 1989 Westmoreland et al.
nC4H5+C2H2=A1+H 2.94E+16 -1.09 9257. ! 2007 Senosiain and Miller
nC4H5+C2H2=fulvene+H 1.52E+15 -0.76 8762. ! 2007 Senosiain and Miller
iC4H5+C2H2=A1+H 1.47E+23 -3.28 24907. ! 2007 Senosiain and Miller
iC4H5+C2H2=fulvene+H 1.01E+34 -5.94 28786. ! 2007 Senosiain and Miller
C3H3+aC3H5=fulvene+2H 3.26E+29 -5.4 3390.0 ! 2009 Hansen et al C3H4 FLAME
fulvene+H=A1+H 3.00E+12 0.5 2000.0 ! 2009 Hansen et al C3H4 FLAME
A1-+H(+M)=A1(+M) 1.00E+14 0.0 0.0 !1997 Wang&Frenklach RRKM
LOW / 6.6E+75 -16.30 7000.0/
```

TROE/ 1.0 0.1 584.9 6113.0/

H2/2.0/ CH4/2.0/ C2H6/3.0/

! Reactions of benzyl radical (A1CH2))

A1CH2=C5H5+C2H2 3.00E+12 0.0 70000.0 ! 1994 Colket&Seery /10 for falloff effect

A1CH2=C7H6+H 4.38E+13 0.078 75900.0 ! 2010 toluene pyrolysis model (refit 0.1atm)

A1CH2+H=C7H6+H2 1.00E+12 0.0 0.0 ! EST

A1CH2+H=A1-+CH3 4.5E+58 -11.9 51860.0 ! 2007 Klippenstein

C7H6+H=¿C5H5+C2H2 7.00E+12 0.0 0.0 ! Est from 2009 Carlo Cavallotti $1.06 * 10^{8}T^{1}.35exp(1716/T)$

C7H6=C7H5+H 1.02E116 -28.46 157860 ! 2011 Polino and Cavallotti. 0.1 atm

C7H6=cC5H4+C2H2 1.26E130 -32.19 173970 ! 2011 Polino and Cavallotti. 0.1 atm

C7H6+CH3=C7H5+CH4 1.87E+04 2.724 6008.0 ! 2009 da Silva & Bozzelli-2

C7H6+H=C7H5+H2 1.90E+08 1.847 4965.0 ! 2009 da Silva & Bozzelli-2

C7H5(+M)=C4H2+C3H3(+M) 3.00E+12 -0.075 62300.0 ! 2010 toluene pyrolysis model

LOW /1.00E+45 8.4 47500/

C7H5(+M)=C2H2+C5H3(+M) 2.00E+11 -0.075 62300.0 ! 2010 toluene pyrolysis model

LOW /1.00E+45 8.4 47500/

C3H3+C4H4 = A1CH2 6.53E+5 1.28 -4611.0 ! 1997 Jones et al.

! Reactions of A1CH3

A1CH2+H(+M)=A1CH3(+M) 7.22E+13 0.062 -44 ! 2007 Klippenstein

LOW / 3.02E+136 -33.35 55560 /

TROE / 0.5 600 900 5500/

H2/2/ CH4/2/ C2H6/3/

A1-+CH3(+M)=A1CH3(+M) 2.33e+14 -0.28 -191 ! 2007 Klippenstein

LOW / 6.67E+83 -19.22 14980 /

TROE / 0.0075 1 -1000 50000 /

A1CH3+H=A1CH2+H2 6.47E00 3.98 3394.0 ! 2006 Oehlschlaeger MA.

A1CH3+CH3=A1CH2+CH4 3.160E+11 0.000 9500.00 ! USC Mech V2.0

A1CH3+A1-=A1CH2+A1 2.103E+12 0.000 4400.00 ! USC Mech V2.0

A1CH3+H=A1+CH3 1.930E+06 2.170 4163.00 ! 2001 Tokmakov&Lin

A1CH3+H=A1-+CH4 6.00E-01 5.0 30000.0 ! 2010 toluene pyrolysis model Est.

A1CH3+H=C6H4CH3+H2 6.00E08 1.0 16800.0 ! 2005 Bounaceur et al.

C6H4CH3+H=A1CH3 1.00E14 0.0 0.0 ! 2005 Bounaceur et al.

C6H4CH3+H=A1CH2+H 1.00E13 0.0 0.0 ! 1992 Miller&Melius

nC4H5+aC3H4=A1CH3+H 2.00E11 0.0 3700.0 ! 1988 Kern et al.

nC4H5+pC3H4=A1CH3+H 3.16E11 0.0 3700.0 ! 1984 Cole et al.

!A1C2H reactions

A1C2H-+H(+M)=A1C2H(+M) 1.00E+14 0.0 0.0 ! USC Mech V2.0 (= A1-+H)

LOW/ 6.6E+75 -16.30 7000. /

TROE / 1.0 0.1 584.9 6113. /

H2/2.0/ CH4/2.0/ C2H6/3.0/

A1C2H*+H(+M)=A1C2H(+M) 1.00E+14 0.0 0.0 ! USC Mech V2.0 (= A1-+H)

LOW/ 6.6E+75 -16.30 7000. /

TROE / 1.0 0.1 584.9 6113. /

H2/2.0/ CH4/2.0/ C2H6/3.0/

A1+C2H=A1C2H+H 5.00E+13 0. 0.0 ! 1997 Wang&Frenklach

A1C2H+H=A1C2H*+H2 2.50E+14 0.0 16000.0 ! 1997 Wang&Frenklach

A1C2H+H=A1C2H-+H2 2.50E+14 0.0 16000.0 ! 1997 Wang&Frenklach

A1C2H-+H=A1C2H 8.02E+19 -2.0 1968.0 ! MIT [A1-+H=A1]

A1CH+H=A1CH2 1.00E+13 0.0 0.0 ! MIT EST

A1CH2+H=A1CH+H2 6.03E+13 0.0 15103.0 ! MIT [1992 Baulch et al. CH3+H=HCH(T)+H2]

A1-+C2H2=A1C2H+H 7.50E+26 -4.0 17100.0 ! 1994 Wang&Frenklach

PLOG / 0.026 7.50E+26 -4.0 17100.0/ !

PLOG / 0.118 9.90E+30 -5.07 21100/ !

PLOG / 1 3.30E+33 -5.70 25500/ !

A1-+C4H4=A1C2H+C2H3 3.20E+11 0.0 1350.0 ! MIT [1988 Harris et al.]

nC4H5+C4H2=A1C2H+H 3.16E+11 0.0 1800.0 ! MIT [1984 Cole et al.]

! A1C2H2 reactions

A1-+C2H3=A1CCH2+H 1.80E+31 -4.63 31652.0 ! 1997 Wang&Frenklach RRKM 20 Torr

A1-+C2H3=A1CHCH+H 1.50E+32 -4.91 35504.0 ! 1997 Wang&Frenklach RRKM 20 Torr

A1CHCH+H=A1CCH2+H 2.30E+37 -6.00 35164.0 ! 1997 Wang&Frenklach RRKM 20 Torr

A1-+C2H2=A1CHCH 4.00E+39 -8.94 12000 ! 1994 Wang&Frenklach RRKM

PLOG / 0.013 4.00E+39 -8.94 12000/ !

PLOG / 0.026 7.70E+40 -9.2 13400.0/ !

PLOG / 0.118 9.90E+41 -9.26 15700/ !

PLOG / 1 7.00E+38 -8.02 16400/ !

PLOG / 10 7.90E+29 -5.15 13700/ !

PLOG / 1.0E5 4.00E+7 1.56 3800/ !

A1C2H+H=A1CHCH 5.00E+54 -12.8 17185.0 ! 1994 Wang&Frenklach *5

A1C2H+H=A1CCH2 5.00E+54 -12.8 17185.0 ! 1994 Wang&Frenklach *5

A1CHCH+H=A1C2H+H2 1.50E+13 0.0 0.0 ! 1997 Wang&Frenklach

A1CCH2+H=A1C2H+H2 3.00E+13 0.0 0.0 ! 1997 Wang&Frenklach

! A1C2H3 reactions

A1+C2H3=A1C2H3+H 35.90E+11 0.0 6400.0 ! 1997 Wang&Frenklach *5

A1-+C2H4=A1C2H3+H 5.10E+12 0.0 6190.0 ! 1997 Wang&Frenklach *2

A1-+C2H3=A1C2H3 1.90E+48 -10.52 17489.0 ! 1997 Wang&Frenklach RRKM

PLOG / 0.026 1.90E+48 -10.52 17489.0/ !

PLOG / 0.118 3.90E+38 -7.63 12900/ !

PLOG / 1 1.20E+27 -4.22 7200/ !

A1C2H3=A1CCH2+H 6.00E+46 -9.07 118323.0 ! 1997 Wang&Frenklach *5

A1C2H3+H=A1CCH2+H2 3.33E+05 2.53 9240.0 ! 1997 Wang&Frenklach

A1C2H3=A1CHCH+H 9.50E+54 -11.39 130224.0 ! 1997 Wang&Frenklach *5

A1C2H3+H=A1CHCH+H2 6.65E+05 2.53 12240.0 ! 1997 Wang&Frenklach

! A1C2H4 reactions

A1-+C2H4=A1CH2CH2 1.00E+40 -9.2 13400.0 ! 1994 Wang&Frenklach A1-+C2H2=A1CHCH /7.7

A1CHCH3=A1CH2CH2 6.40E+61 -14.59 88200.0 ! Ref: pC3H4 = aC3H4 (0.1ATM WH)1999 Davis et al.

A1CH2CH2+H=A1CHCH3+H 2.30E+37 -6.00 35164. ! Ref: A1CHCH+H=A1CCH2+H

A1CHCH3=A1C2H3+H 9.00E+12 0.00 50669.0 ! 1988 Mueller-Markgraf&Troe fall-off /3

A1CH2CH2=A1C2H3+H 5.00E+12 0.0 50669.0 ! Est

A1CHCH3+H=A1C2H3+H2 2.00E+12 0.00 0.0 ! C2H5+H=C2H4+H2 GRI

A1CH2CH2+H=A1C2H3+H2 2.00E+12 0.00 0.0 ! C2H5+H=C2H4+H2 GRI

C4H4+C4H4=A1C2H3 0.75E+14 0.0 38000.0 ! MIT[1984 Lundgard&Heicklen] /2

C6H4C2H4+H=A1CH2CH2 3.00E+13 0.0 0.0 ! Est 2011 Li et al.(Toluene)

C6H4C2H4=o-C6H4+C2H4 6.50E+13 0.0 83000.0 ! Ref to o-C6H4=C4H2+C2H2

! A1C2H5 reactions

A1-+C2H5(+M)=A1C2H5(+M) 2.33E+14 -0.283 -191.0 ! Ref A1-+CH3=A1CH3 (2007 Klippenstein)

LOW/ 6.73E83 -19.22 14980.0/

TROE/ 0.5918 320.14 1858.22 5394.9928/

A1CHCH3+H(+M)=A1C2H5(+M) 7.22E+13 0.062 -44.0 ! Ref A1CH2+H=A1CH3 (2007 Klippenstein)

LOW/ 3.02E136 -33.35 55560.0 /

TROE/ 2.545 2.156 453.23 4551.5/

A1CH2CH2+H(+M)=A1C2H5 (+M) 5.21E+17 -0.990 1580.0 ! Ref C2H5+H=C2H6 (GRI)

LOW/ 1.990E+41 -7.080 6685.00 /

TROE/ 0.8422 125.0 2219.00 6882.0 /

H2/2.0/ CH4/2.0/ C2H6/3.0/ AR/0.7/

A1C2H5=A1CH2+CH3 6.11E+96 -23.78 118160 !

PLOG / 0.039 6.11E+96 -23.78 118160/ ! Ref to A1C3H7=A1CH2+C2H5, 2013 Wang et al.

PLOG / 1.0E+5 8.91E+15 0.00 74720/ ! 2012 Darcy et al.

A1C2H5+H=A1CHCH3+H2 3.31E+07 2.0 5345.3 ! 2005 Baulch et al.

A1C2H5+H=A1CH2CH2+H2 7.22E+08 1.50 7412.0 ! 2005 Baulch et al.

A1C2H5+H=A1+C2H5 5.78E+13 0 8087.0 ! 2005 Baulch et al.

! C9H7 and C9H8 reactions

! C7H6+C2H2=C9H8 1.44E+292 -78.2 245010.0 ! 2009 da Silva & Bozzelli-1

! C7H6+C2H2=C9H7+H 9.70E-42 16.7 37520.0 ! 2009 da Silva & Bozzelli-1

! A1CH2+C2H2=C9H8+H 3.16E+04 2.5 11061.2 ! 2009 Blanquart et al.

! A1-+aC3H4=C9H8+H 5.13E+02 3.2 2788.0 ! 2003 Vereecken et al.

! A1-+C3H3=C9H8 1.50E+75 -17.8 39600.0 ! Est. ref: A1-+C4H3=A2 (MIT)

! A1+C3H3=C9H8+H 6.26E+09 2.61 56500.0 ! 2010 toluene pyrolysis model

! C9H7+H(+M)= C9H8 (+M) 1.00E+14 0.0 0.0 ! REF: C5H5+H=C5H6 in USC Mech V2.0 1992 Emdee et al., est., 1994 Frank et al.

! LOW / 4.400E+81 -18.280 12994.0/ !

! TROE / 0.068 400.7 4135.8 5501.9 /

! H2/2.0/ CH4/2.0/

! C9H8+H=C9H7+H2 2.80e+13 0.0 2258.6 ! 2009 Blanquart et al.

! C9H8+CH3¡=¿C9H7+CH4 1.80E-01 4.0 456.5 ! 2009 Blanquart et al.

!***********135TCH sub reaction*****************this work*******

!C9

! 135trimethylcyclohexane reactions-cis

! isomerization and decomposition of 135trimethylcyclohexane

T135CH=S1X35DCH+CH3 2.26E+16 0 84525.6 !barierlessRxn!mrci

T135CH=T135CH-bi 6.36E+15 0 86741.3 !mrci

T135CH-t=T135CH-bi 1.46E+16 0 88356.9 !mrci

T135CH-bi=C7H12-2E46M-t 8.30E+10 0 2189.7 !casscf

T135CH-bi=C7H12-1E46M 1.45E+10 0 8763.2 !casscf

T135CH-bi=C7H12-1E24M 8.41E+10 0 4491.9 !casscf

! CH3-abstractions of 135trimethylcyclohexane

T135CH+H = S1X35DCH+CH4 2.54E+14 0 36421.4

! H-abstractions of methylcyclohexane

T135CH+H = P1XCH235DCH+H2 1.24E+15 0 13584.3

T135CH+H = S2X135TCH+H2 9.02E+14 0 11014.1

T135CH+H = T1X135TCH+H2 4.46E+14 0 8387.8

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T135CH+CH3 = P1XCH235DCH+CH4 4.56E+12 0 18963.5
T135CH+CH3 = S2X135TCH+CH4 3.76E+12 0 16397.4
T135CH+CH3 = T1X135TCH+CH4 4.47E+12 0 14157.6
!cyclohexyl radicals
!P1XCH235DCH = CH2-35DCH+H 5.60E+13 0 37846.2
P1XCH235DCH = P7XC7H11-1E46M 3.32E+14 0 32329.8
P1XCH235DCH = S2X135TCH 9.75E+12 0 50041.7
S2X135TCH = D35CH-1E+CH3 4.01E+14 0 31596.5
S2X135TCH = T135CH-1E+H 1.24E+14 0 36954.0
S2X135TCH = P7XC7H11-2E46M-t 1.65E+14 0 31205.0
T1X135TCH = T135CH-1E+H 2.68E+14 0 37641.5
T1X135TCH = S6XC7H11-1E24M 1.93E+14 0 30887.0
S1X35DCH = D35CH-1E+H 2.54E+14 0 38321.2
S1X35DCH = S6XC7H12-1E4M 1.54E+14 0 30310.8
!cyclohexene dissociation
T135CH-1E = C3H6+C5H7-13E2M 1.15E+15 0 64679.4 !reverseDA
T135CH-1E+H = S6X135TCH-1E+H2 2.68E+14 0 8395.3
T135CH-1E+CH3 = S6X135TCH-1E+CH4 1.84E+12 0 13694.0
T135CH-1E+H = T3X135TCH-1E+H2 2.06E+14 0 5440.6
T135CH-1E+CH3 = T3X135TCH-1E+CH4 2.74E+12 0 10922.8
S6X135TCH-1E = D13CH-15E+CH3 1.44E+15 0 44229.1
D13CH-15E+H = T3X13DCH-15E+H2 5.53E+14 0 4488.1
D13CH-15E+CH3 = T3X13DCH-15E+CH4 2.05E+12 0 10701.1
D13CH-15E+H = S4X13DCH-15E+H2 3.18E+14 0 6787.3
D13CH-15E+CH3 = S4X13DCH-15E+CH4 2.69E+12 0 12317.3
T3X13DCH-15E = m-xylene+H 7.16E+13 0 31054.0
S4X13DCH-15E = A1CH3+CH3 1.18E+14 0 24081.0
S4X13DCH-15E = m-xylene+H 4.13E+13 0 29037.0
T3X135TCH-1E = T135CH-13E+H 9.63E+13 0 50520.6 !barierlessRxn
T135CH-13E+H = S6X135TCH-13E+H2 3.62E+14 0 6714.0
T135CH-13E+CH3 = S6X135TCH-13E+CH4 4.48E+12 0 10400.6
S6X135TCH-13E = m-xylene+CH3 1.38E+14 0 24259.7
m-xylene+H=A1CH3+CH3 1.93E+06 4.5 4163.00 !  2001 Tokmakov&Lin !n value change in this work
D35CH-1E = C3H6+C5H8-13E 1.32E+15 0 63850.7 !!reverseDA
D35CH-1E+H = S6X35DCH-1E+H2 2.77E+14 0 8768.1
D35CH-1E+CH3 = S6X35DCH-1E+CH4 6.05E+12 0 14023.3
D35CH-1E+H = T3X35DCH-1E+H2 1.73E+14 0 5810.8
D35CH-1E+CH3 = T3X35DCH-1E+CH4 3.00E+12 0 11080.8
S6X35DCH-1E = MCH-35E+CH3 1.56E+15 0 44298.7
```

MCH-35E+H = T1XMCH-35E+H2 3.43E+14 0 5026.4
MCH-35E+CH3 = T1XMCH-35E+CH4 1.99E+12 0 10714.0
T1XMCH-35E = A1CH3+H 2.77E+13 0 30426.0
MCH-35E+H = S2XMCH-35E+H2 3.07E+14 0 6775.4
MCH-35E+CH3 = S2XMCH-35E+CH4 3.50E+12 0 12193.3
S2XMCH-35E = A1+CH3 2.93E+14 0 24625.4
S2XMCH-35E = A1CH3+H 5.67E+13 0 29746.4
T3X35DCH-1E = D13CH-15E+H 1.25E+14 0 51019.4 !barierlessRxn
!TCH isomer
D13CH+H = S1X35DCH+H2 3.41E+14 0 11222.3
D13CH+CH3 = S1X35DCH+CH4 1.52E+12 0 16667.2
S1X35DCH = S2X35DCH 3.09E+13 0 43108.3
T124CH+H = S2X35DCH+CH4 8.74E+13 0 36224.7
D13CH+H = T3X13DCH+H2 3.22E+14 0 8568.4
D13CH+CH3 = T3X13DCH+CH4 2.30E+12 0 14155.4
T133CH+H = T3X13DCH+CH4 8.49E+13 0 34521.6
D13CH+H = S3XMCH+CH4 1.79E+14 0 36485.0
MEtCH = T1XMCH+C2H5 4.32E+15 0 73776.8 !barrierless
! alkenes reactions
C7H12-2E46M-t = iC4H9+S4XC5H9-2E 1.39E+15 0 66583.1 !barrierless
C7H12-2E46M-t+H = T4XC7H11-2E46M-t+H2 1.27E+14 0 8878.8
C7H12-2E46M-t+CH3 = T4XC7H11-2E46M-t+CH4 6.76E+10 0 12537.4
C7H12-2E46M-t = iC4H10+C5H8-13E 9.59E+14 0 111676.7
C7H12-2E46M-t = iC4H8+C5H10-2E 3.34E+15 0 105683.3
C7H12-1E46M = S2XC5H102M+aC3H5 6.34E+14 0 62968.4 !barrierless
C7H12-1E46M+H = S3XC7H11-1E46M+H2 2.09E+14 0 8248.3
C7H12-1E46M+CH3 = S3XC7H11-1E46M+CH4 3.49E+11 0 12737.2
C7H12-1E46M = C3H6+C5H9-1E4M 5.21E+14 0 104528.7
C7H12-1E46M = C3H6+C5H9-2E4M 1.99E+15 0 103580.8
C7H12-1E24M = S2XC5H11+iC4H7 2.88E+15 0 65989.0 !barrierless
C7H12-1E24M+H = S3XC7H11-1E24M+H2 1.53E+14 0 7935.9
C7H12-1E24M+CH3 = S3XC7H11-1E24M+CH4 2.55E+11 0 13102.2
C7H12-1E24M = C5H10-1E+iC4H8 6.37E+14 0 107422.1
C7H12-1E24M = C5H10-2E+iC4H8 1.87E+15 0 106356.9
! Alkenyl RAdical reactions
S6XC7H12-1E4M = T4XC7H12-1E4M 5.90E+12 0 38907.4
S6XC7H12-1E4M = S5XC7H12-1E4M 2.28E+13 0 41524.5
S6XC7H12-1E4M = S3XC7H12-1E4M 1.42E+12 0 17276.3
S6XC7H12-1E4M = P7XC7H12-1E4M 1.69E+13 0 43501.8
T4XC7H12-1E4M = C2H5+C5H7-14E2M 8.28E+20 0 37581.9

T4XC7H12-1E4M = C2H3+C5H9-1E2M 1.76E+21 0 45037.9
S6XC7H12-1E4M = C3H6+S4XC5H9-1E 1.59E+14 0 28176.5
S5XC7H12-1E4M = CH3+C6H9-15E3M 4.19E+16 0 35785.5
S5XC7H12-1E4M = aC3H5+C5H10-2E 1.22E+16 0 25231.5
S3XC7H12-1E4M = nC3H7+C5H8-13E 1.11E+15 0 38794.1
P7XC7H12-1E4M = C2H4+P5XC5H8-1E4M 4.16E+14 0 30821.5
S6XC7H12-1E4M = P1XCH2cC5H724M 8.28E+10 0 4607.1
S6XC7H11-1E24M = T4XC7H11-1E24M 1.85E+13 0 41820.6
S6XC7H11-1E24M = S5XC7H11-1E24M 3.81E+13 0 44326.5
S6XC7H11-1E24M = S3XC7H11-1E24M 6.91E+11 0 17916.4
S6XC7H11-1E24M = P7XC7H11-1E24M 1.06E+07 0 36282.3
T4XC7H11-1E24M = CH3CCH2+C5H9-1E2M 7.39E+14 0 34821.7
T4XC7H11-1E24M = C2H5+C5H6-14E24M 8.38E+13 0 29070.7
S6XC7H11-1E24M = C3H6+S4XC5H8-1E2M 2.81E+14 0 29498.0
S5XC7H11-1E24M = iC4H7+C5H10-2E 2.88E+16 0 25485.8
S5XC7H11-1E24M = CH3+C6H8-15E24M 1.95E+17 0 37049.4
!S3XC7H11-1E24M = CH3+C7H11-13E2M 1.19E+14 0 38601.4
S3XC7H11-1E24M = nC3H7+C5H7-13E2M 1.10E+14 0 36141.2
P7XC7H11-1E24M = C2H4+P5XC5H7-1E24M 4.32E+14 0 30330.6
S6XC7H11-1E24M = P1XCH2cC5H6124M 6.09E+10 0 6753.3
P7XC7H11-1E46M = T6XC7H11-1E46M 1.65E+13 0 37190.4
P7XC7H11-1E46M = T4XC7H11-1E46M 3.63E+12 0 17701.4
P7XC7H11-1E46M = S5XC7H11-1E46M 1.55E+13 0 37442.8
P7XC7H11-1E46M = S3XC7H11-1E46M 3.56E+11 0 7612.0
T6XC7H11-1E46M = iC4H8+S4XC5H9-1E 2.87E+19 0 35239.0
T4XC7H11-1E46M = C2H3+C5H8-1E24M 1.80E+21 0 47380.8
T4XC7H11-1E46M = iC3H7+C5H7-14E2M 7.63E+20 0 36787.0
S5XC7H11-1E46M = CH3+C7H11-15E4M 1.07E+14 0 31656.1
S5XC7H11-1E46M = aC3H5+C5H9-2E4M 1.55E+13 0 20150.2
!S3XC7H11-1E46M = CH3+C7H11-13E6M 4.39E+14 0 38525.8
S3XC7H11-1E46M = iC4H9+C5H8-13E 2.25E+14 0 37544.2
P7XC7H11-1E46M = C3H6+P5XC5H8-1E4M 1.25E+14 0 27936.1
P7XC7H11-2E46M-t = T6XC7H11-2E46M-t 3.79E+13 0 35948.4
P7XC7H11-2E46M-t = T4XC7H11-2E46M-t 1.69E+12 0 14705.1
P7XC7H11-2E46M-t = S5XC7H11-2E46M-t 2.12E+13 0 39525.4
T6XC7H11-2E46M-t = iC4H8+S4XC5H9-2E 3.19E+13 0 20515.9
T4XC7H11-2E46M-t = iC3H7+C5H7-13E2M 7.07E+15 0 39290.9
S5XC7H11-2E46M-t = CH3+C7H11-25E4M 8.51E+13 0 32009.8
S5XC7H11-2E46M-t = CH3+C7H11-24E6M 4.74E+13 0 28619.7
S5XC7H11-2E46M-t = CH3CHCH+C5H9-2E4M 1.53E+14 0 38199.9

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!P7XC7H11-2E46M-t = C3H6+P5XC5H8-2E4M 1.99E+14 0 27842.7
P7XC7H11-2E46M-t = S2XC2H4cC5H735M 3.01E+11 0 5421.9
! clyclopantane reactions
S2XC2H4cC5H735M = T3XcC5H635M1Et 2.61E+11 0 23866.3
T3XcC5H635M1Et = S5XC7H11-1E24M 5.75E+13 0 33575.7
!T3XcC5H635M1Et = cC5H5-3E35M1Et+H 3.33E+14 0 39032.6
!cC5H5-3E35M1Et+H = S2XcC5H4-3E35MEt+H2 2.51E+14 0 7230.2
!cC5H5-3E35M1Et+CH3 = S2XcC5H4-3E35MEt+CH4 1.42E+12 0 12673.0
!cC5H5-3E35M1Et+H = T5XcC5H4-3E35MEt+H2 1.66E+14 0 7118.2
!cC5H5-3E35M1Et+CH3 = T5XcC5H4-3E35MEt+CH4 1.42E+12 0 11431.6
!cC5H5-3E35M1Et+H = S5XcC5H5-3E3M1Et+CH4 9.92E+13 0 32383.4
!S2XcC5H4-3E35MEt = cC5H4-13E25M+C2H5 4.33E+14 0 37657.4
!T5XcC5H4-3E35MEt = cC5H4-13E13M+C2H5 5.61E+14 0 38410.6
!S5XcC5H5-3E3M1Et = cC5H5-13E1M+C2H5 4.34E+14 0 38472.2
!cC5H4-13E25M+H = T2XcC5H4-13E5M+CH4 3.42E+14 0 43038.8
!cC5H5-13E5M+H = T2XcC5H4-13E5M+H2 4.12E+14 0 20162.1
!cC5H5-13E5M+CH3 = T2XcC5H4-13E5M+CH4 3.58E+12 0 22370.0
!cC5H4-13E13M+H = T3XcC5H4-13E1M+CH4 3.71E+14 0 43026.9
!cC5H5-13E1M+H = T3XcC5H4-13E1M+H2 4.38E+14 0 20116.4
!cC5H5-13E1M+CH3 = T3XcC5H4-13E1M+CH4 3.82E+12 0 22393.8
P1XCH2cC5H724M = T4XcC5H6124M 1.05E+12 0 23001.8
!T4XcC5H6124M = S5XC6H9-1E24M 7.44E+13 0 34160.0
T4XcC5H6124M = cC5H5-3E135M+H 2.32E+14 0 39229.3
cC5H5-3E135M+H = S2XcC5H4-3E135M+H2 2.58E+14 0 7393.0
cC5H5-3E135M+CH3 = S2XcC5H4-3E135M+CH4 1.42E+12 0 12961.3
cC5H5-3E135M+H = T5XcC5H4-3E135M+H2 1.73E+14 0 7204.0
cC5H5-3E135M+CH3 = T5XcC5H4-3E135M+CH4 1.40E+12 0 10944.3
cC5H5-3E135M+H = S5XcC5H5-3E13M+CH4 9.69E+13 0 30506.6
S2XcC5H4-3E135M = cC5H4-13E35M+CH3 5.54E+14 0 39903.0
T5XcC5H4-3E135M = cC5H4-13E13M+CH3 5.21E+14 0 39996.4
S5XcC5H5-3E13M = cC5H5-13E1M+CH3 4.55E+14 0 40129.5
cC5H4-13E35M+H = T2XcC5H4-13E5M+CH4 3.42E+14 0 41038.8
!P1XCH2cC5H6124M = T4XcC5H51124M 2.23E+12 0 21827.4
!T4XcC5H51124M = cC5H4-1E1344M+H 4.01E+14 0 38905.4
!T4XcC5H51124M = cC5H4-3E1355M+H 7.42E+14 0 37941.6
!cC5H4-1E1344M+H = S3XcC5H4-1E144M+CH4 9.13E+13 0 32389.4
!S3XcC5H4-1E144M = cC5H4-13E14M+CH3 6.02E+14 0 39712.2
!cC5H4-3E1355M+H = S2XcC5H3-3E1355M+H2 2.47E+14 0 7432.1
!cC5H4-3E1355M+CH3 = S2XcC5H3-3E1355M+CH4 1.52E+12 0 13062.5
!S2XcC5H3-3E1355M = cC5H2-13E1355M+H 1.32E+14 0 45383.7
```

```
!cC5H4-13E14M+H = T4XcC5H4-13E1M+CH4 1.18E+14 0 42859.9
!cC5H5-13E1M+H = T4XcC5H4-13E1M+H2 5.27E+14 0 20416.5
!cC5H5-13E1M+CH3 = T4XcC5H4-13E1M+CH4 4.74E+12 0 22544.8
cC5H5-13E5M = cC5H5-13E1M 1.50E+13 0 24466.4
C5H5+CH3 = cC5H5-13E5M 8.34E+15 -0.74 -0.50 !J. Phys. Chem. A,2009, 113, 8871-8882
! 135trimethylcyclohexane reactions-trans
! CH3-abstractions of 135trimethylcyclohexane
T135CH-t+H = S1X35DCH+CH4 1.05E+14 0 36022.0
T135CH-t+H = S1X35DCH-t+CH4 1.69E+14 0 36272.4
! H-abstractions of methylcyclohexane
T135CH-t+H = P1XCH235DCH-t+H2 5.44E+14 0 13481.6
T135CH-t+H = P3XCH235DCH-t+H2 9.85E+14 0 13578.9
T135CH-t+H = S2X135TCH-t+H2 5.47E+14 0 11294.8
T135CH-t+H = S4X135TCH-t+H2 2.97E+14 0 10941.9
T135CH-t+H = T1X135TCH+H2 1.71E+14 0 8051.7
T135CH-t+H = T3X135TCH-t+H2 2.35E+14 0 8694.0
T135CH-t+CH3 = P1XCH235DCH-t+CH4 1.91E+12 0 18854.8
T135CH-t+CH3 = P3XCH235DCH-t+CH4 2.96E+12 0 18956.9
T135CH-t+CH3 = S2X135TCH-t+CH4 8.38E+11 0 16669.2
T135CH-t+CH3 = S4X135TCH-t+CH4 1.06E+12 0 16352.5
T135CH-t+CH3 = T1X135TCH+CH4 7.78E+11 0 13817.8
T135CH-t+CH3 = T3X135TCH-t+CH4 1.65E+11 0 14629.4
! isomerization and decomposition of 135trimethylcyclohexane
T135CH-t = S1X35DCH+CH3 8.70E+16 0 81691.8 !barrierless !mrci
T135CH-t = S1X35DCH-t+CH3 5.98E+16 0 84010.9 !barrierless !mrci
!cyclohexyl radicals
!P1XCH235DCH-t = CH2-35DCH+H 9.38E+13 0 36534.7
P1XCH235DCH-t = P7XC7H11-1E46M 1.55E+14 0 31556.7
P1XCH235DCH-t = S2X135TCH-t 2.90E+13 0 42754.6
S2X135TCH-t = D35CH-1E+CH3 2.07E+14 0 31695.8
S2X135TCH-t = D35CH-1E-t+CH3 1.87E+14 0 30833.4
S2X135TCH-t = T135CH-1E+H 8.43E+13 0 33816.2
S2X135TCH-t = P7XC7H11-2E46M-t 8.24E+13 0 31441.5
S4X135TCH-t = P7XC7H11-2E46M-t 7.60E+13 0 30575.1
S4X135TCH-t = T135CH-3E-t+H 6.81E+13 0 35823.3
S4X135TCH-t = D35CH-1E-t+CH3 2.48E+14 0 33003.4
T3X135TCH-t = T135CH-3E-t+H 2.02E+14 0 37174.6
T3X135TCH-t = S6XC7H11-1E24M 1.01E+14 0 29649.0
P3XCH235DCH-t = P7XC7H11-1E46M 1.35E+14 0 32019.8
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P3XCH235DCH-t = S2X135TCH-t 9.98E+12 0 50031.7

S1X35DCH-t = D35CH-1E-t+H 2.16E+14 0 38323.2

S1X35DCH-t = S6XC7H12-1E4M 7.54E+13 0 29299.3

T135CH-3E-t = C3H6+C5H7-13E2M 5.39E+14 0 63189.0 !reverseDA

D35CH-1E-t = C3H6+C5H8-13E 9.51E+14 0 62714.0 !!reverseDA

!DCH-trans formation

D13CH-t+H = S1X35DCH-t+H2 3.36E+14 0 11044.5

D13CH-t+CH3 = S1X35DCH-t+CH4 2.80E+12 0 16434.3

! reactions of C5H7-13E2M & C5H7-14E2M

C5H7-13E2M+H = C3H6+CH3CHCH 1.46E+30 -4.34 21647.0 !C4H5-13E2M+H = C3H6+C2H3 ! =(C4H6+H) JetSurF 2.0 !

C5H7-13E2M+H = CH3CCH2+C3H6 1.46E+30 -4.34 21647.0 !C4H5-13E2M+H = CH3CCH2+C2H4! =(C4H6+H) !

C5H7-13E2M+H = C5H8-13E+CH3 8.00E+21 -1.79 11180.0 !C4H5-13E2M+H = C4H6+CH3! 1991 TSA RRKM 1 atm JetSurF 2.0 ! n value

C5H7-14E2M+H = C5H8-14E+CH3 8.00E+21 -1.79 11180.0 !C4H5-13E2M+H = C4H6+CH3! 1991 TSA RRKM 1 atm JetSurF 2.0 ! n value

C5H7-14E2M+H = iC4H7+C2H4 1.60E+22 -2.39 11180.0 !C5H8-14E+H = aC3H5+C2H4 ! = C3H6+H JetSurF 2.0

C5H7-14E2M+H = C4H5-13E2M+CH3 2.00E+12 0.0 7000. !C5H8-14E+H = C4H6+CH3 ! =(C4H6+H) JetSurF 2.0

C5H7-13E2M = C5H7-14E2M 1.1E+13 0.00 67000.0 ! similar C5H8-12E = C5H8-13E

PLOG / 0.039 1.1E+13 0.00 67000.0 / ! /20 EST

PLOG / 1.0 2.20E+14 0.00 67000.0/ ! JetSurF 2.0

S4XC5H8-1E2M = C5H7-13E2M+H 1.27E+24 -4.75 23777 ! Ref to C4H7 = C4H6+H

PLOG / 0.033 1.27E+24 -4.75 23777/

PLOG / 0.066 1.38E+26 -5.221 25729/

PLOG / 0.132 1.75E+28 -5.709 27764/

PLOG / 0.197 3.16E+29 -6.003 28985/

PLOG / 0.263 2.69E+30 -6.222 29890/

PLOG / 1.0 2.48E+53 -12.30 52000/

PLOG / 10 1.85E+48 -10.50 51770/

! others

C5H9-1E4M=aC3H5+iC3H7 1.07E+80 -19.33 95177 ! Ref to C6H12-1E=aC3H5+nC3H7 !

PLOG / 0.039 1.07E+80 -19.33 95177/

PLOG / 0.066 2.50E+68 -16.040 86832/

PLOG / 0.132 1.480E+59 -13.261 82596/

```
PLOG / 0.197 2.43E+61 -13.999 82637/
PLOG / 0.263 3.75E+59 -13.427 82179/
PLOG / 1.0E+5 1.46E+16 0.00 69120/
C5H9-1E4M=S4XC5H9-1E+CH3 2.7E+80 -1.93E+01 1.07E+05 ! Ref to C6H12-1E=C4H7+C2H5
PLOG / 0.033 2.7E+80 -19.331 107015/
PLOG / 0.066 6.27E+68 -16.040 98670/
PLOG / 0.132 3.70E+59 -13.261 94434/
PLOG / 0.197 6.08E+61 -13.999 94475/
PLOG / 0.263 9.38E+59 -13.427 94017/
PLOG / 1.0E+5 1.46E+16 0 81020/
C5H9-1E4M = C3H6+C3H6 8.0E+05 1.81 53454 !
PLOG / 0.039 8.0E+05 1.81 53454/ ! 1.62E+06 /20 EST
PLOG / 1 1.62E+06 1.81 53454/ ! 08/TSAwip JetSurF 2.0
END
```

4.5.3 Experimental Data

Verious experimental paremeter.

Table 4.9: Dwell time, pressure, temperature and initial concentration of 135TCH used in the shock tube experiment.

SL No	**Dwell Time** (ms)	**Pressure** (P_5) bar	**Temperature** (T_5) K	$[T135CH]_0$	$[T135CH]_t$
1	1.48	22.55	1458	0.005974154	0.001137934
2	1.4	21.54	1482	0.005793502	0.001103524
3	1.48	18.35	1364	0.006051702	0.001152705
4	1.42	17.18	1317	0.006105454	0.001162944
5	1.45	15.87	1197	0.002702099	0.000514685
6	1.46	15.17	1176	0.003116621	0.000593642
7	1.48	14.12	1101	0.002179343	0.000415113
8	1.51	11.87	1066	0.001977352	0.000376638
9	1.54	15.62	1300	0.002772504	0.000528096
10	1.46	18.14	1240	0.006766446	0.001288847
11	1.46	14.38	1119	0.00459205	0.000874676
12	1.48	14.64	1137	0.003443392	0.000655884
13	1.44	16.86	1157	0.007948123	0.001513928
14	1.47	19.96	1384	0.005611402	0.001068838
15	1.44	20.49	1436	0.003183505	0.000606382
16	1.46	19.39	1394	0.005840551	0.001112486
17	1.4	23.46	1542	0.002701959	0.000514659
18	1.44	24.85	1517	0.004497555	0.000856677
19	1.46	14.95	1119	0.005342174	0.001017557
20	1.4	16.72	1291	0.003645064	0.000694298
21	1.46	22.35	1529	0.003903503	0.000743524
22	1.41	13.35	1017	0.001943687	0.000370226

Table 4.10: Mole fraction of various products and reactant after pyrolysis.

SL No	**Methane**	**Ethylene**	**Acetylene**	**Ethane**	**Propene**	**Allene**
1	0.18882	0.13021	0.10674	0.01587	0.10101	0.00623
2	0.20554	0.10446	0.14404	0.01909	0.11317	0.00746
3	0.12713	0.08650	0.08678	0.01996	0.06446	0.00653
4	0.10329	0.07351	0.04734	0.02754	0.07519	0.00709
5	0.05364	0.04121	0.01694	0.03146	0.06358	0.00589
6	0.04091	0.02891	0.00895	0.02503	0.04874	0.00401
7	0.01305	0.00666	0.00076	0.00561	0.01151	0.00106
8	0.00244	0.00000	0.00000	0.00000	0.00000	0.00000
9	0.11685	0.08388	0.04508	0.04007	0.09678	0.00984
10	0.04869	0.03939	0.01987	0.02439	0.04487	0.00494
11	0.01431	0.00816	0.00177	0.00791	0.01953	0.00129
12	0.02192	0.01100	0.00267	0.01180	0.02794	0.00202
13	0.02372	0.01616	0.00506	0.01506	0.03097	0.00239
14	0.15157	0.09033	0.08700	0.01914	0.09183	0.00697
15	0.23390	0.13536	0.12874	0.03000	0.12100	0.01011
16	0.16167	0.10440	0.10933	0.02098	0.07830	0.00746
17	0.27181	0.15515	0.20185	0.03346	0.10685	0.00938
18	0.22388	0.10752	0.17315	0.01933	0.10911	0.00719
19	0.00913	0.00420	0.00116	0.00381	0.01102	0.00076
20	0.07672	0.05094	0.02215	0.02175	0.07566	0.00627
21	0.23738	0.11091	0.17905	0.02159	0.11904	0.00764
22	0.00234	0.00000	0.00000	0.00000	0.00000	0.00000

SL No	**Propyne**	**Butene**	**Vinylacetylene**	**1,3-butadiene**	**1,3-butadiyne**	**2-butayne**	**1,3-butadiene,2-methyl**
1	0.02023	0.00253	0.00577	0.03354	0.00065	0.00073	0.00000
2	0.01342	0.00453	0.01173	0.03289	0.00073	0.00055	0.00000
3	0.01223	0.00259	0.00518	0.02280	0.00032	0.00032	0.00058
4	0.01224	0.00264	0.00626	0.02526	0.00028	0.00048	0.00092
5	0.00805	0.00239	0.00689	0.02298	0.00045	0.00053	0.00086
6	0.00572	0.00160	0.00528	0.01642	0.00033	0.00052	0.00043
7	0.00139	0.00000	0.00123	0.00257	0.00000	0.00000	0.00000
8	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
9	0.01508	0.00410	0.00778	0.03397	0.00042	0.00053	0.00083
10	0.00678	0.00112	0.00373	0.01756	0.00021	0.00048	0.00064
11	0.00157	0.00069	0.00194	0.00487	0.00000	0.00000	0.00000
12	0.00248	0.00089	0.00302	0.00760	0.00000	0.00000	0.00000
13	0.00305	0.00102	0.00336	0.00897	0.00018	0.00028	0.00035
14	0.01276	0.00400	0.00852	0.02586	0.00044	0.00064	0.00070
15	0.01764	0.00404	0.01333	0.04261	0.00084	0.00104	0.00134
16	0.01386	0.00300	0.00669	0.02681	0.00037	0.00046	0.00067
17	0.01707	0.00343	0.00849	0.04477	0.00085	0.00050	0.00094
18	0.01352	0.00418	0.01122	0.03147	0.00065	0.00032	0.00082
19	0.00106	0.00025	0.00084	0.00230	0.00000	0.00000	0.00000
20	0.00972	0.00261	0.00594	0.02357	0.00033	0.00043	0.00068
21	0.01399	0.00478	0.01330	0.03472	0.00115	0.00051	0.00091
22	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

SL No	**1-butyne**	**1,4-pentadiene**	**1,3-pentadiene**	**1,3-cyclopentadiene**	**1,4-pentadiene, 3-methyl**
1	0.00331	0.00865	0.00755	0.00700	0.00124
2	0.00143	0.01558	0.00966	0.01001	0.00103
3	0.00162	0.00989	0.00597	0.00682	0.00119
4	0.00075	0.01079	0.00659	0.00775	0.00123
5	0.00000	0.01006	0.00707	0.00718	0.00124
6	0.00000	0.00862	0.00601	0.00618	0.00000
7	0.00000	0.00000	0.00000	0.00000	0.00000
8	0.00000	0.00000	0.00000	0.00000	0.00000
9	0.00046	0.01365	0.00815	0.01018	0.00079
10	0.00023	0.00564	0.00394	0.00537	0.00000
11	0.00000	0.00416	0.00269	0.00217	0.00000
12	0.00000	0.00556	0.00370	0.00250	0.00000
13	0.00000	0.00479	0.00335	0.00303	0.00056
14	0.00186	0.01499	0.00877	0.00799	0.00156
15	0.00303	0.01583	0.00977	0.01351	0.00155
16	0.00217	0.01108	0.00659	0.00761	0.00081
17	0.00063	0.00989	0.00570	0.01497	0.00062
18	0.00461	0.01586	0.00976	0.01135	0.00117
19	0.00000	0.00137	0.00115	0.00070	0.00000
20	0.00023	0.01203	0.00699	0.00699	0.00083
21	0.00472	0.01681	0.01028	0.01155	0.00119
22	0.00000	0.00000	0.00000	0.00000	0.00000

SL No	**1,3-pentadiene,2-methyl**	**1,3-cyclopentadiene,5-methyl**	**1,3-cyclopentadiene,1-methyl**	**Benzene**	**1,3-cyclohexandiene**
1	0.00040	0.00195	0.00188	0.01922	0.00066
2	0.00274	0.00363	0.00101	0.02197	0.00184
3	0.00198	0.00197	0.00068	0.01326	0.00050
4	0.00212	0.00217	0.00069	0.00964	0.00052
5	0.00124	0.00137	0.00000	0.00465	0.00115
6	0.00140	0.00204	0.00000	0.00328	0.00000
7	0.00000	0.00000	0.00000	0.00000	0.00000
8	0.00000	0.00000	0.00000	0.00000	0.00000
9	0.00241	0.00264	0.00083	0.00867	0.00000
10	0.00097	0.00099	0.00042	0.00494	0.00000
11	0.00000	0.00000	0.00000	0.00000	0.00000
12	0.00088	0.00086	0.00000	0.00110	0.00000
13	0.00086	0.00082	0.00021	0.00191	0.00055
14	0.00266	0.00275	0.00078	0.01277	0.00096
15	0.00253	0.00466	0.00147	0.02908	0.00173
16	0.00200	0.00243	0.00067	0.01793	0.00074
17	0.00138	0.00360	0.00119	0.03879	0.00133
18	0.00288	0.00431	0.00127	0.02548	0.00181
19	0.00000	0.00000	0.00000	0.00082	0.00000
20	0.00199	0.00188	0.00062	0.00469	0.00059
21	0.00291	0.00426	0.00134	0.02539	0.00189
22	0.00000	0.00000	0.00000	0.00000	0.00000

SL No	**Toluene**	**1,3-dimethyl-cyclohexane**	**1,3-dimethyl-cyclohexane-trans**	**T135CH**	**T135CH-t**
1	0.00552	0.00573	0.00084	0.27033	0.05232
2	0.00581	0.00365	0.00091	0.21666	0.04429
3	0.00292	0.00372	0.00073	0.42052	0.08778
4	0.00293	0.00428	0.00073	0.46493	0.09725
5	0.00165	0.00000	0.00000	0.58893	0.11495
6	0.00000	0.00000	0.00000	0.65085	0.13212
7	0.00000	0.00000	0.00000	0.79753	0.15862
8	0.00000	0.00000	0.00000	0.83078	0.16678
9	0.00200	0.00352	0.00119	0.41346	0.07683
10	0.00147	0.00132	0.00000	0.62437	0.13310
11	0.00000	0.00000	0.00000	0.77390	0.15039
12	0.00000	0.00174	0.00000	0.73366	0.15475
13	0.00076	0.00077	0.00000	0.71847	0.14824
14	0.00377	0.00451	0.00089	0.36264	0.07077
15	0.00919	0.00165	0.00000	0.13413	0.02794
16	0.00418	0.00447	0.00062	0.32965	0.07044
17	0.01067	0.00000	0.00000	0.03853	0.00829
18	0.00811	0.00251	0.00050	0.16644	0.03545
19	0.00082	0.00116	0.00000	0.78978	0.16396
20	0.00135	0.00393	0.00000	0.54088	0.11449
21	0.00750	0.00214	0.00000	0.13313	0.02689
22	0.00000	0.00000	0.00000	0.83393	0.16373

SL No	1,1,3-dimethyl-cyclohexane	Styrene	1,2,4-dimethyl-cyclohexane	1-methyl,1-ethyl-cyclohexane
1	0.00000	0.00000	0.00105	2.58E-05
2	0.00000	0.00000	0.00214	3.28E-05
3	0.00161	0.00000	0.00341	2.73E-05
4	0.00266	0.00000	0.00289	3.36E-05
5	0.00000	0.00189	0.00375	0.00E+00
6	0.00000	0.00000	0.00265	0.00E+00
7	0.00000	0.00000	0.00000	0.00E+00
8	0.00000	0.00000	0.00000	0.00E+00
9	0.00000	0.00000	0.00000	0.00E+00
10	0.00000	0.00000	0.00454	4.65E-05
11	0.00000	0.00000	0.00465	0.00E+00
12	0.00000	0.00000	0.00390	0.00E+00
13	0.00000	0.00000	0.00513	0.00E+00
14	0.00159	0.00099	0.00000	0.00E+00
15	0.00274	0.00116	0.00000	7.17E-05
16	0.00263	0.00103	0.00090	3.58E-05
17	0.00187	0.00159	0.00638	0.00E+00
18	0.00302	0.00107	0.00205	0.00E+00
19	0.00000	0.00000	0.00571	0.00E+00
20	0.00222	0.00000	0.00338	1.40E-04
21	0.00208	0.00111	0.00183	0.00E+00
22	0.00000	0.00000	0.00000	0.00E+00

Chapter 5

Theoretical Kinetic Study of Thermal Decomposition of Decalin

5.1 Introduction

Decalin is the simplest bicyclic cyclohexane, an important component in the traditional aviation, diesel fuel[1], and in the new fuels source like diesel from direct coal liquefaction (DDLC)[2] and oil sand[3]. Decalin is two fused cyclohexane rings. Trans decalin has been selected as the surrogate component for investigation of transportation fuel[4]. There are many previous experimental studies on pyrolysis/ oxidation of decalin, summarized in table 1.9. Experimentally it is difficult to identify the initial decomposition process of decalin. Here, theoretical studies can be of great value. However, to the best of our knowledge, a detailed theoretical investigation on decalin has not been carried out. Two previous theoretical studies on decalin[5,6] did not focus on initial unimolecular decomposition mechanism.

Initial unimolecular decomposition reaction of cycloalkanes is a significant step in pyrolysis/combustion/oxidation of cycloalkanes. For example, the initial reaction of alkylcyclohexane may proceed via the dissociation of C-H bond, elimination of side-chain alkyl group, or isomerization via ring-opening leading to alkene. Understanding of initial unimolecular reaction is important to develop complete pyrolysis/oxidation kinetic models of cycloalkane.Moreover, the competition between ring-opening isomerization and C-H elimination channel has a significant effect on aromatic formation. Several Studies on unimolecular reaction of cyclohexane/methylcyclohexane are available in the literature and there is disagreement between these studies about the initial process. Tsang[7] and Brown et al.[8] proposed that the initial decomposition of cyclohexane was formation of 1-hexene via ring-opening. However 1-hexene was not detected during the pyrolysis/oxidation of cyclohexane carried out by Aribike et al.[9,10], Voisin et al.[11], and EI Bakali et al.[12]. They proposed other initial dissociation channels of cyclohexane (Aribike et al.: $cC_6H_{12} = 3C_2H_4$, $cC_6H_{12} = 2C_3H_6$, $cC_6H_{12} = C_4H_6 + C_2H_4 + H_2$; Voisin et al.: $cC_6H_{12} = cC_6H_{11} + H$; El Bakali et al.: $cC_6H_{12} = C_2H_4 + C_4H_8$). Finally, Kiefer et al.[13] studied the pyrolysis of cyclohexane in shock tube and theoretically calculated the reaction pathways for cyclohexane dissociation. Their theoretical calculation confirms that the initial decomposition of cyclohexane produces 1-hexene. A similar disagreement was observed for the initial decomposition of methylcyclohexane[14–16] as well.

This discrepancy for the initial reaction of cyclohexane/methylcyclohexane as well as no details thermal decomposition study of decalin avalable in the literature motivate us to theoretically study the thermal decomposition of decalin. A detailed investigation on thermal decomposition of decalin would help in understanding the effect of unimolecular decomposition mechanism as well as aromatic formation during pyrolysis. In this work, we report results from a detailed theoretical investigation of thermal decomposition of decalin using high level of quantum chemical calculation. TST/VTST calculations have been used to obtain reliable rate constants for all important elementary reactions associated with decalin decomposition.

5.2 Computational Details

5.2.1 Geometry optimization and frequency calculation

The initial ring-opening path of decalin is associated with unstable biradical intermediate, and the decomposition path involve C-C bond lengthening during the bond dissociation (figure). To calculate the accurate energy barrier for these steps, one needs the multireference method as involved biradical possesses multireference characteristics. Geometry optimizations and frequency calculation for biradicals have been carried out using CASSCF method with the basis set of 6-31+g(d,p). A minimum active space (i.e.,CAS(2e,2o) has been chosen for $C - H$ loss reaction channels as well as isomerization channels. Single-point energies have been corrected using the MRCI method with the same active space and basis set. The zero-point energy (ZPE) scaling factor for the CASSCF method is 0.93[16]. For all other types of reaction single reference method has been used. In this work, we were using CBS-QB3 method (section 2.2.1.1). IRC calculations were done with the same method to confirm that transition state connect with the reactant(s) and product(s). All multireference calculations were performed using Molpro 2018 program while Gaussian 16 program was used for CBS-QB3 calculation.

5.2.2 Reaction rate calculation

We calculated high-pressure limit rate in this work as described in details at section 2.2.3.1.

Kinetic parameters A and E_a to be used in chemical kinetic modeling, were obtained by fitting the calculated rate constant over the 800-2000 K temperature range to Arrhenius expression.

$$k(T) = A\exp(-E_a/RT)$$

As we are getting good fitting with temperature coefficient, n=0 in our considered temperature range, the temperature co-efficient has been taken as zero. All the rate calculations were performed using the multiwell 2020 program.

5.3 Results and discussion

The thermal decomposition of decalin can be classified in seven classes of reactions as given below:

i) Unimolecular decomposition and isomerization of decalin

ii) H-abstraction reaction by H atom and CH_3 radical

iii) Dissociation and isomerization of decalin radical

iv) Decomposition and isomerization of alkenylcyclohexane radicals

v) Decomposition and isomerization of alkenyl radicals

vi) Dissociation of alkenecyclohexane
and
vii) Stepwise dehydrogenation of cyclic intermediate.

The global scheme of thermal decomposition of decalin is shown in figure 5.1. The initial reaction involves the C-C bond dissociation from side-chain $C-H$ group to form decalin radical (by H atom elimination) as well as ring opening of cyclohexane group to form olefinic intermediate. Then, chain reactions occur through the H-abstraction from three different C atoms within decalin by H atom and CH_3 radical. The H-abstraction reactions result in formation of three types of decalin radicals which can either isomerize to form alkenylcyclohexane radical or form cyclic intermediate/aromatic by sidewise dehydrogenation. Alkenylcyclohexane radicals isomerization into alkenyl radicals and methylhydrindane radicals.

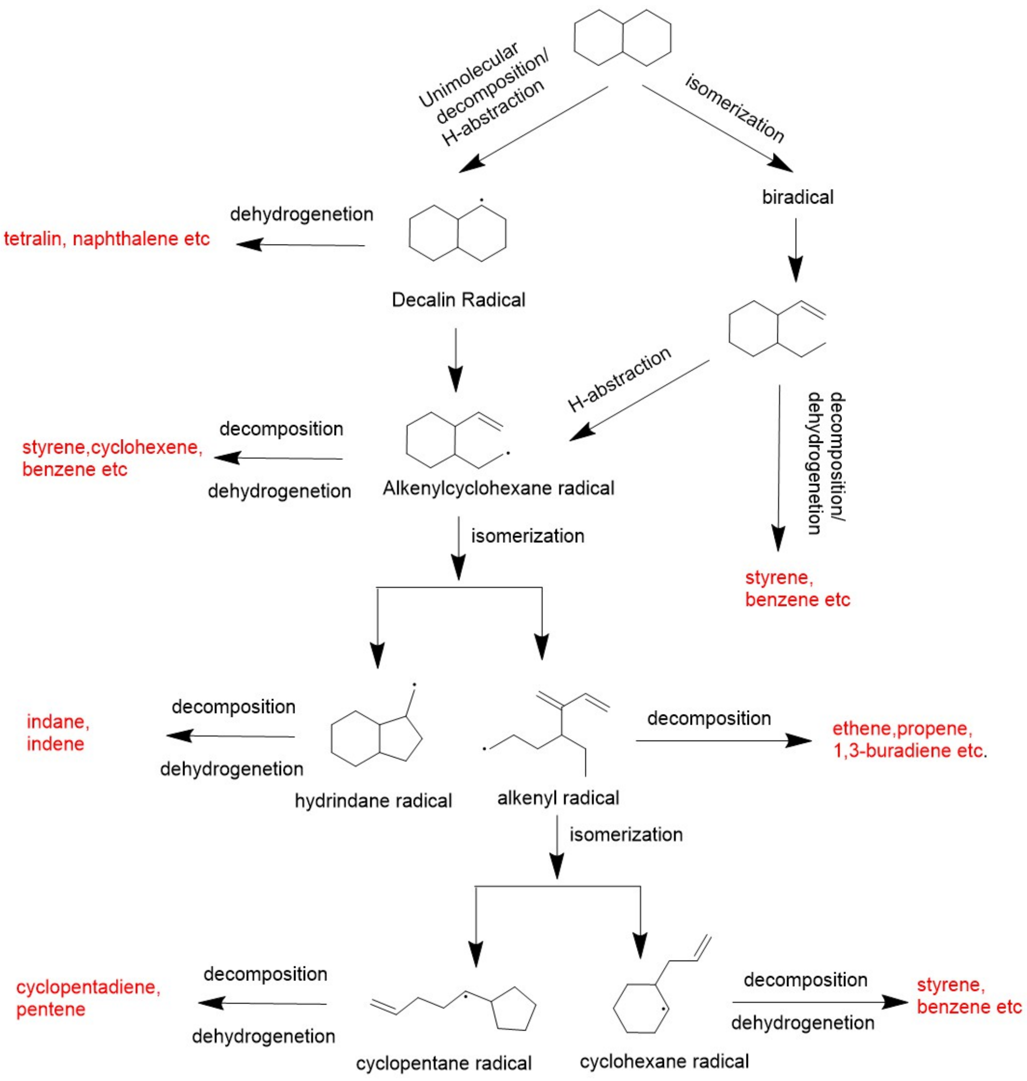

Figure 5.1: Global reaction scheme of decalin thermal decomposition.

(secondary reactions). Alkenyl radicals decompose into small molecules and radicals (secondary reactions) or isomerize into cyclohexane/cyclopentane radicals. In the following sections, we have first discussed the potential energy surface (PES) and analyzed the reaction mechanism of all kinds of reaction classes mentioned above. Thereafter, the rate parameters associated with each of the reactions involved have been discussed further.

5.3.1 Potential energy surface and analysis of reaction mechanism

We started our calculations with the lowest energy confirmer (i.e. trans chair confirmer) based on the CBS-QB3 level.

5.3.1.1 Unimolecular decomposition and isomerization of decalin

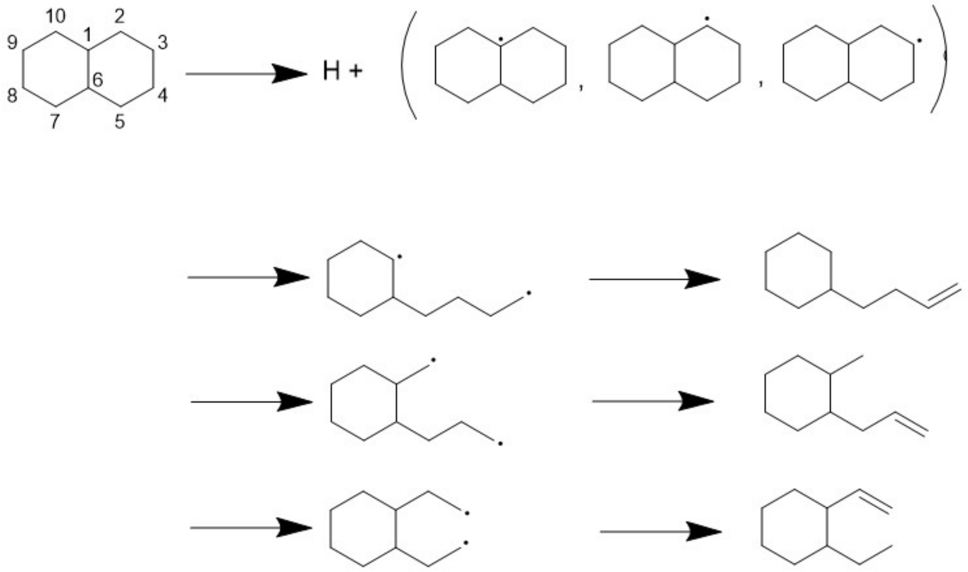

Figure 5.2: Decomposition and isomerization of decalin.

In figure 5.2, we showed all the possible reaction channels of the initial decomposition and isomerization pathways of decalin. In this process, three decalin radicals, and olefinic intermediate (through three different biradicals) are formed. We used the multireference method to calculate PES for these processes. Initial decomposition of decalin has no saddle point along the reaction coordinate and the reverse reaction is barrier-less process.

Figure 5.3 shows the calculated potential energy surface at MRCI//CAS(2,2)/6-31+g(d,p) (red colour) and CAS(2,2)/6-31+g(d,p) (black colour) level of theory. The PES shows that the ring opening isomerization channels are more energetically favorable than the initial decomposition channels. In the first step, one of the cyclohexane ring-opens with C-C bond dissociation and forming a biradical. In the next step, H-migration happens, and an alkene is formed. Decalin has three unique ring C-C bonds (C1-C2, C2-C3, and C3-C4), the dissociation of each (by ring-opening) can generate altogether three biradicals (biradical1, biradical2, and biradical3).

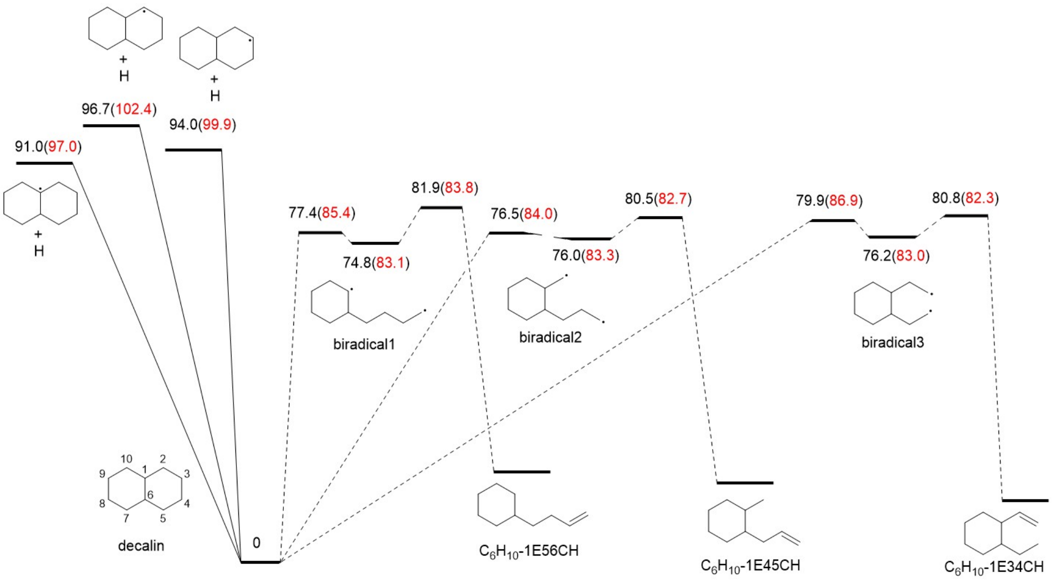

Figure 5.3: Potential energy surface for initial decomposition (C1-H,C2-H, and C3-H bond dissociation) and ring opening isomerization (ring C1-C2, C2-C3, and C3-C4 bond dissociation) of decalin. Methods were MRCI/6-31+g(d,p)//CAS(2,2)/ 6-31+g(d,p) (value in the bracket with red colure) and CAS(2,2)/ 6-31+g(d,p) (value with black colour). Energy unit: kcal/mol. .

Table 5.1: Comparison of relative energy of initial decomposition and isomerization channel of cyclohexane, methylcyclohexane and decalin. Energy unit: kcal/mol.

	cyclohexane[13]	methylcyclohexane[16] (method:MRCI)	decalin (method:MRCI)
$C-H$ bond diss.	97.8	-	97.0/102.4/99.9
$C-CH_3$ bond diss.	-	84.0	-
TS of C1-C2 ring opening	88.7 (CASPT2 /cc-pVDZ)	85.0	85.4
TS of C2-C3 ring opening	-	89.0	84.0
TS of C3-C4 ring opening	-	89.0	86.9

C2-C3 ring-opening isomerization channel (formation of biradical2) is the most energetically favorable isomerization channel. H-migration from biradical to form alkene involves a 6-member cyclic transition state. Among the three initial decompostion channels, C1-H dissociation leads to a tertiary radical is energitically favourable one. In Table 5.1, we compare the energy barrier of decalin with cyclohexane[13] and methylcyclohexane[16]. We can see that C-H bond dissociation energy is higher than C-CH3 bond dissociation. Ring-opening energy barrier are comparable for all of them.

5.3.1.2 H-abstraction reaction by H atom and CH_3 radical

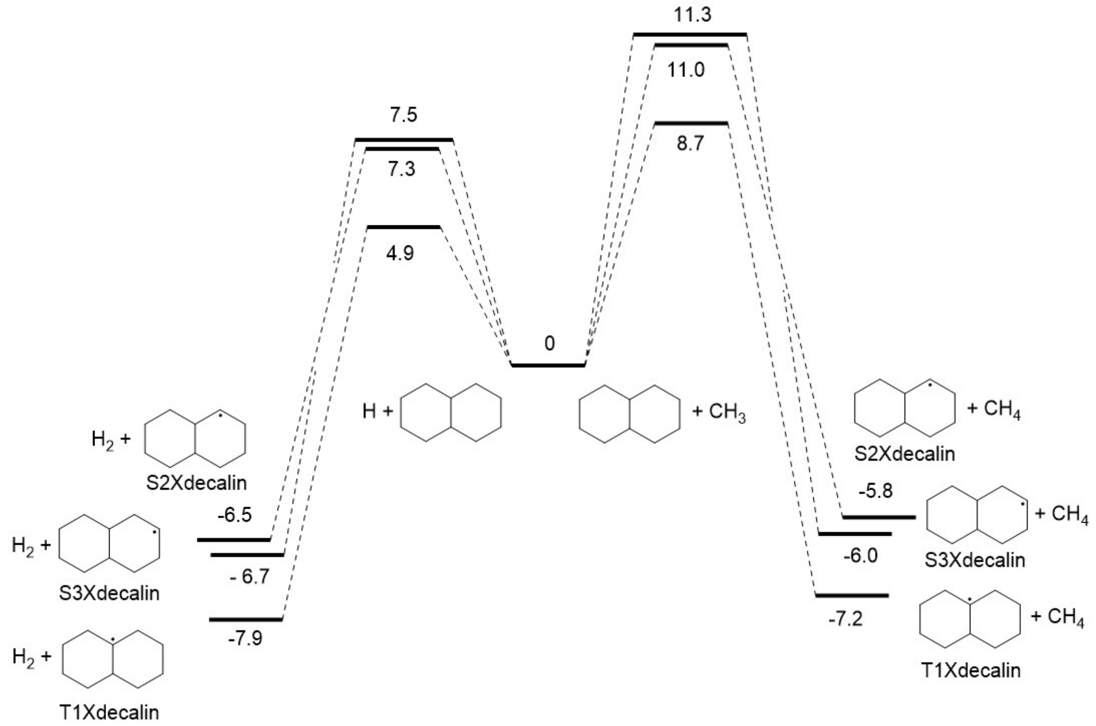

Figure 5.4: Potential energy surface for H-atom abstraction reactions of decalin by H atom and CH_3 radical. Energy unit: kcal/mol.

Except unimolecular decomposition and isomerization of decalin, we have used CBS-QB3 level of theory for all other classes of reactions. As mentioned earlier, decalin has three different C atoms, so three different decalin radicals can be formed (through H- abstraction reaction by H atom/CH_3 radical). Figure 5.4 shows the potential energy surface for these types of reactions.

The energy barrier for H-abstraction by H atom is less compared to H-abstraction by CH_3 radical. The energy barrier for these type of reactions (abstractions) is low. It follows the order: H-abstraction at the secondary carbon >H-abstraction at the tertiary carbon.

In Table 5.2, we compare the energy barrier of the H-abstraction reaction of methylcyclohexane and decalin by H atom.

Table 5.2: Comparison of energy barrier of H-abstraction reaction by H atom between methylcyclohexane and decalin. Energy unit: kcal/mol. Method: CBS-QB3.

	methylcyclohexane[17]	decalin
Primary carbon H-abstraction	9.9	-
C1(H) abstraction	4.9	4.9
C2(H) abstraction	7.3	7.3
C3(H) abstraction	7.2	7.5
C4(H) abstraction	7.2	-

5.3.1.3 Dissociation and isomerization of decalin radical

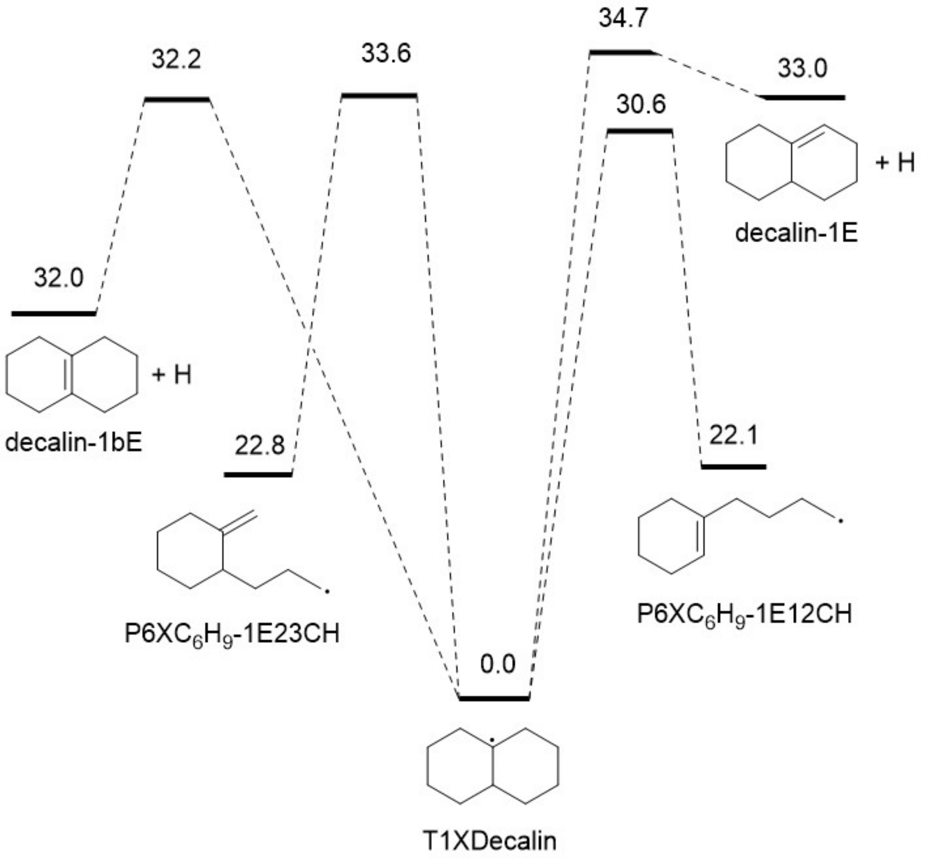

Figure 5.5: Isomerization and decomposition reactions of T1Xdecalin. Energy unit: kcal/mol.

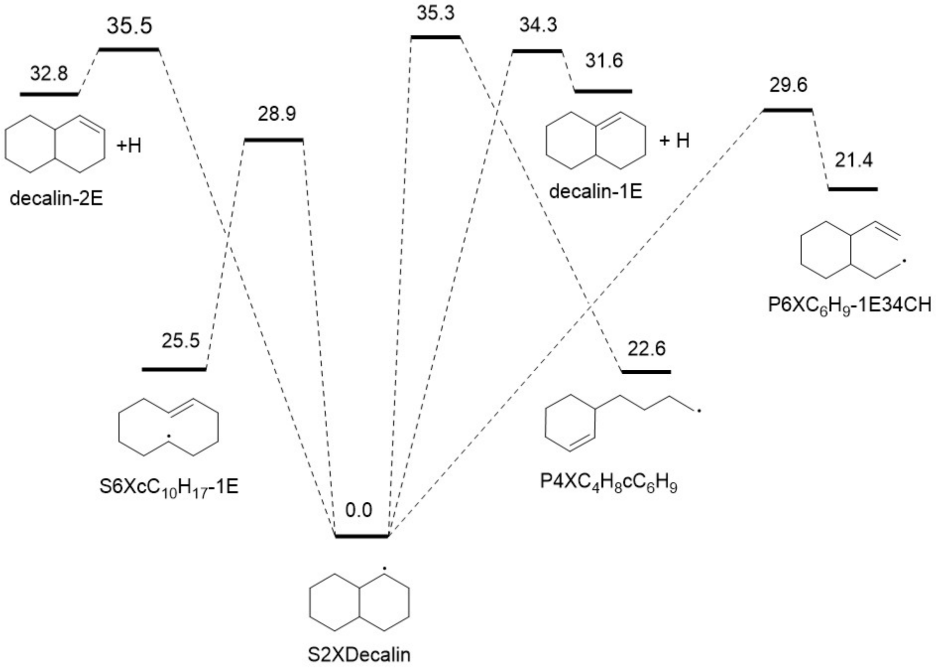

Figure 5.6: Isomerization and decomposition reactions of S2Xdecalin.

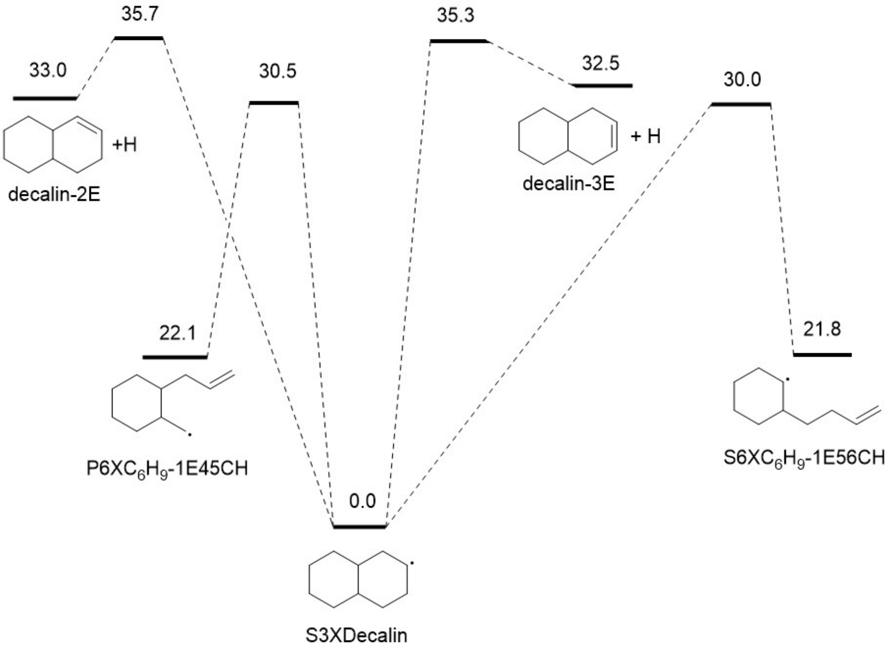

Figure 5.7: Isomerization and decomposition reactions of S3Xdecalin.

As shown in figure 5.4, the H-abstraction reaction leads to decalin radicals.

These radicals can further undergo either H-elimination or isomerization. Figure 5.5, 5.6 and 5.7 show all these reactions of all decalin radicals. It can be seen that the dissociation occurs via $\beta - C - H$ scission and while isomerization takes place via $\beta - C - C$ scission to open the one six-member ring. The energy barrier for the isomerization process is lower than those of H-elimination pathways for S2Xdecalin and S3Xdecalin, whereas H-elimination has lower barrier path for T1Xdecalin. This characteristics for decalin radical is different from methylcyclohexane radical. For methylcyclohexane radical, ring-opening isomerization process always has the lower barrier[17]. The energetics corresponding to ring opening isomerization path for decalin radical and methylcyclohexane radical have been compared in the table 5.3, shown below:

Table 5.3: Comparison between ring-opening isomerization of decalin radical and methylcyclohexane radical. Energy unit: kcal/mol. MCH-methylcyclohexane.

Similar structure	C-C bond dissociation	MCH[17]	decalin
C1 carbon radical centre	adjacent to tertiary carbon centre	-	30.6
	far to tertiary carbon centre	29.6	33.6
C2 carbon radical centre	adjacent to tertiary carbon centre	28.9	28.9,35.5
	far to tertiary carbon centre	29.5	29.6
C3 carbon radical centre	adjacent to tertiary carbon centre	28.7	30.0
	far to tertiary carbon centre	29.7	30.5
C4 carbon radical centre	One unique C-C bond	30.2	-

For ring-opening isomerization, C-C bond dissociation adjacent to tertiary carbon centre has a lower energy barrier than the other one for decalin radical. There is a similar trend for MCH radical as well. Table 5.4 shows the comparison of lowest energy path of methylcylcohexane radical and decalin radical.

Table 5.4: Lowest energy pathway comparison between decalin radical. Energy unit: kcal/mol

	Bond dissociation	Energy barrier
MCH[17]	isomerization via $\beta - C - C$ scission	28.6
decalin	isomerization via $\beta - C - C$ scission	28.9

5.3.1.4 Decomposition and isomerization of alkenylcyclohexane radicals

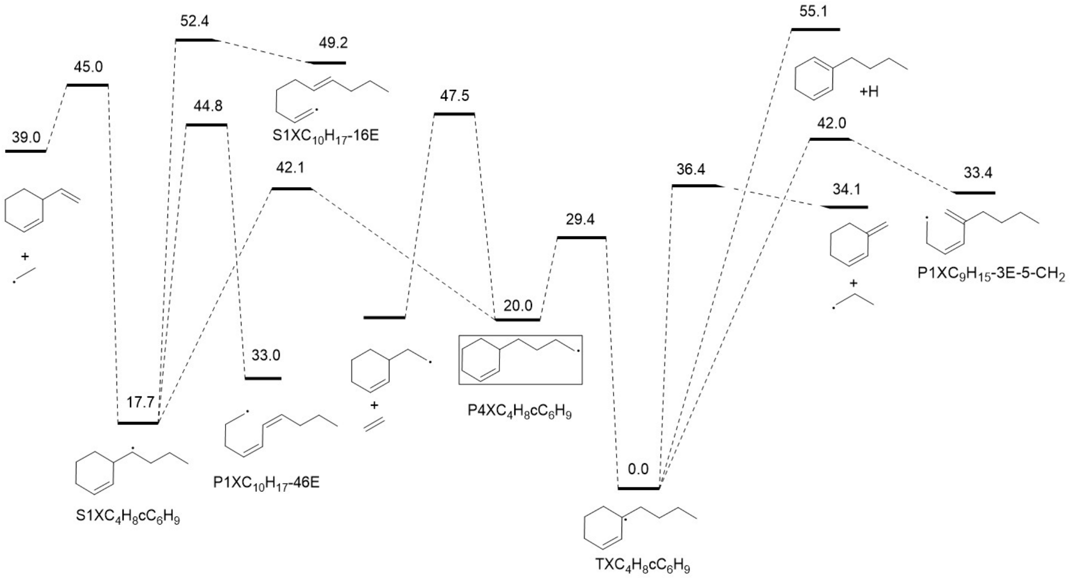

Figure 5.8: Isomerization and decomposition reactions of $P4XC_4H_8cC_6H_9$.

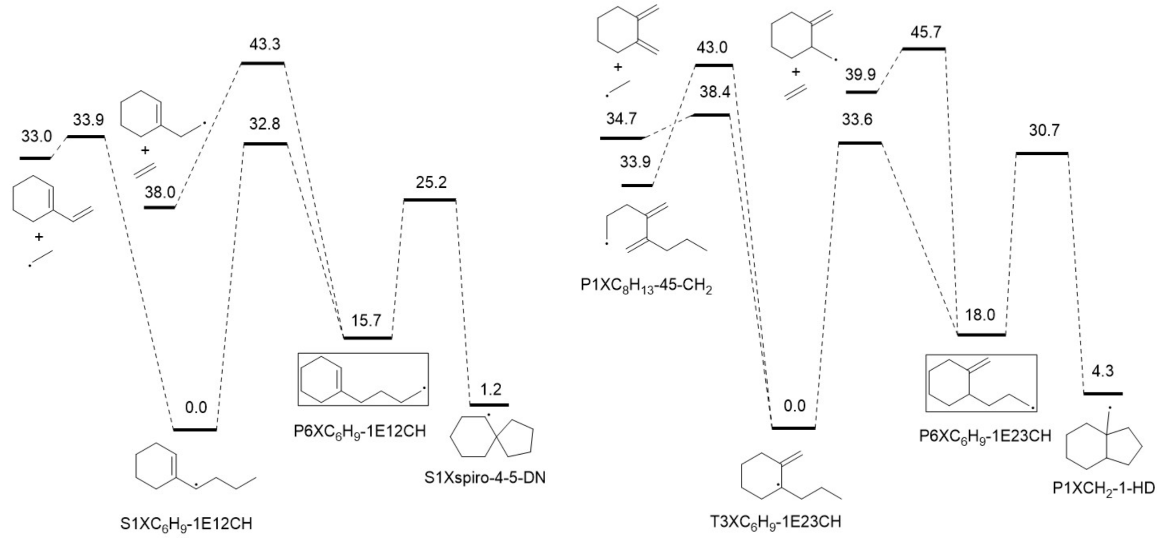

Figure 5.9: Isomerization and decomposition reactions of $P6XC_6H_9 - 1E12CH$ and $P6XC_6H_9 - 1E23CH$.

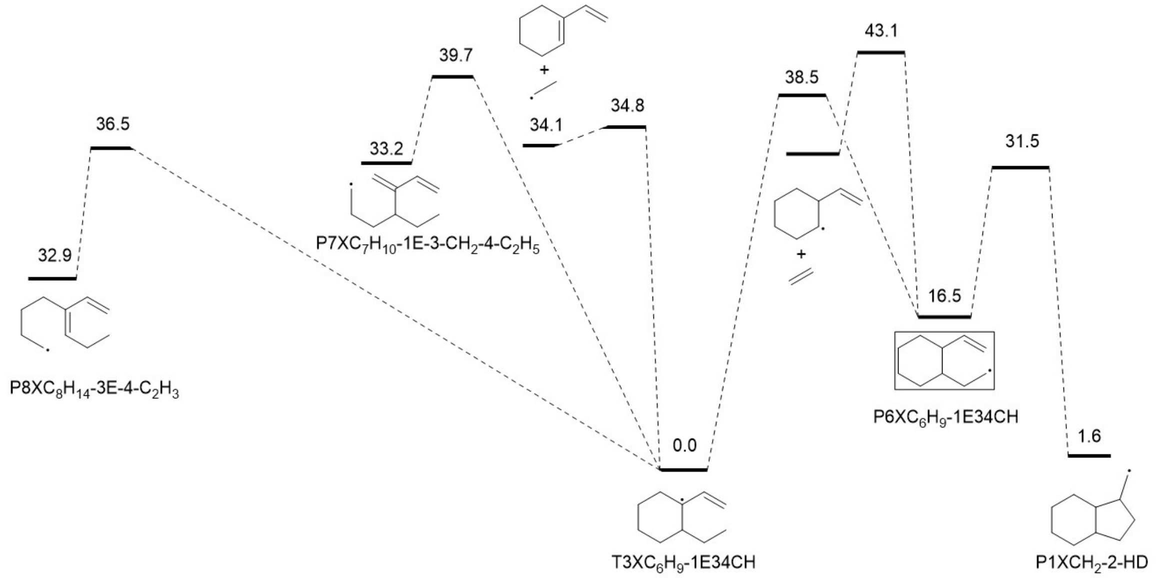

Figure 5.10: Isomerization and decomposition reactions of $P6XC_6H_9 - 1E34CH$.

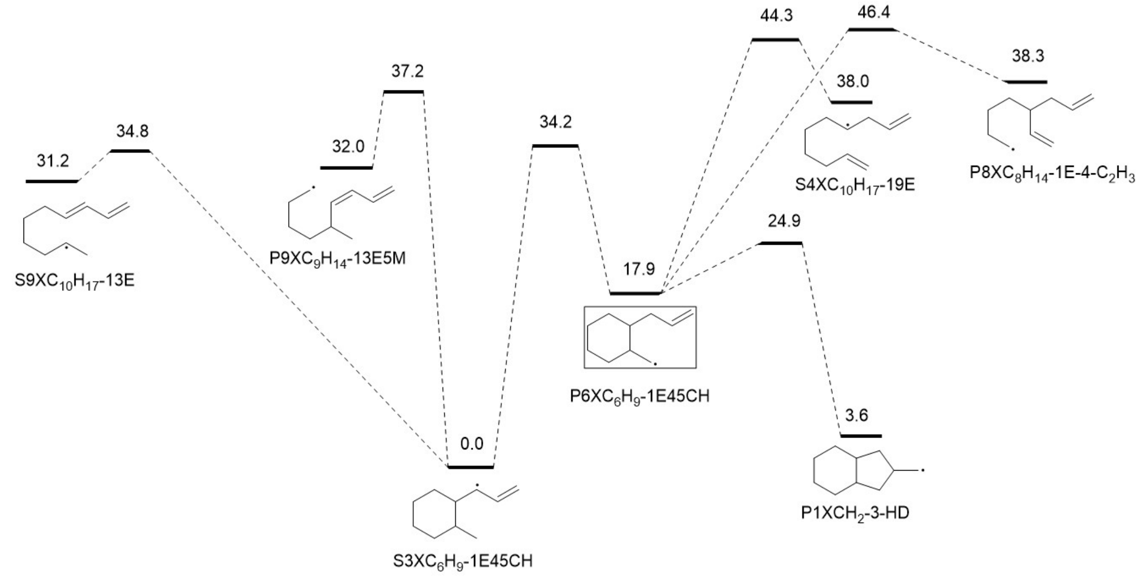

Figure 5.11: Isomerization and decomposition reactions of $P6XC_6H_9 - 1E45CH$.

The ring-opening isomerization of decalin radical forms alkenylcyclohexane radicals. Compared to alkylcyclohexane radicals, reaction pathways of alkenylcyclohexane radical and their rate constant have not been fully investigated. For alkenylcyclohexane radicals, two types of reactions are commonly considered, in-

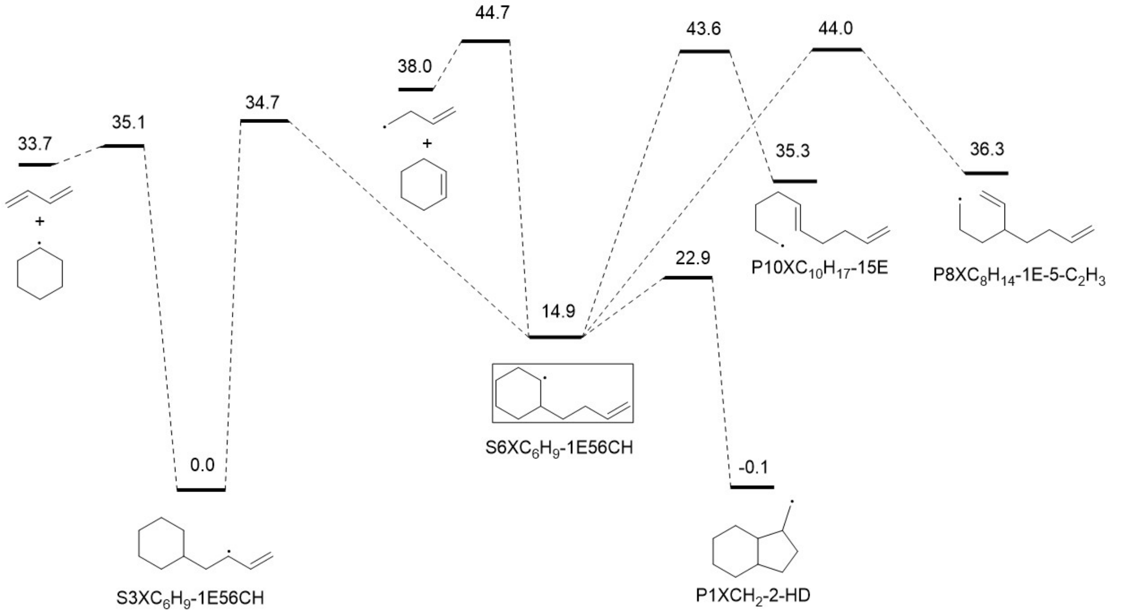

Figure 5.12: Isomerization and decomposition reactions of $S6XC_6H_9-1E56CH$.

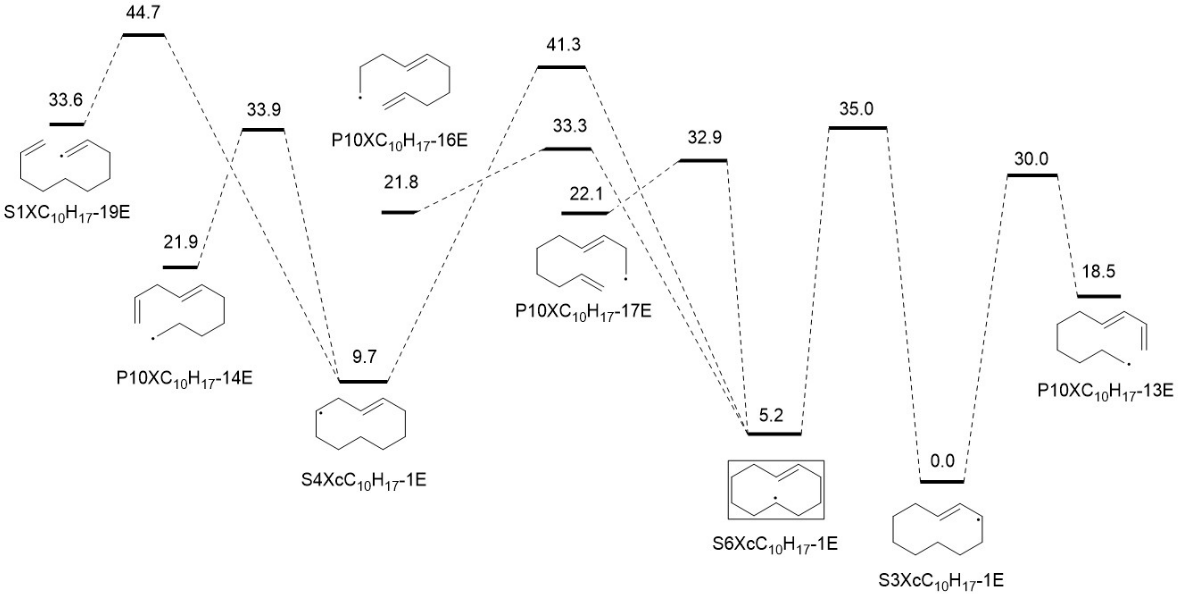

Figure 5.13: Isomerization and decomposition reactions of $S6XcC_{10}H_{17}-1E$.

tramolecular H-shift and $\beta-C-C$ scission. In our study, we only consider two types of intramolecular H-shift pathways. These are 1,4-H shift and 1,5-H shift. 1,4-H shift (undergoes via 5-member ring TS) and 1,5-H shift (undergoes via 6-

member ring TS) have relatively less energy barrier compared to other intramolecular H-shift pathways. Figure 5.8, 5.9, 5.10, 5.11, 5.12 and 5.13 show all these reactions of all alkenylcyclohexane radicals. Ring-opening $\beta - C - C$ scission of leads to alkenyl radicals whereas $\beta - C - C$ scission also leads to smaller intermediates. For few alkenylcyclohexane radicals ring-closing reaction (between radical carbon center and C-C double bond) can lead to methyldydrindane radicals and spiro-4-5-decane radical. Ring closing reaction of P6XC6H9-1E12CH leads to spiro-4-5-decane radical whereas ring closing reaction of P6XC6H9-1E23CH, P6XC6H9-1E34CH, P6XC6H9-1E45, and S6XC6H9-1E56 leads to different methyldydrindane radicals.

5.3.1.5 Decomposition and isomerization of alkenyl radicals

Different alkenyl radicals are formed by ring-opening isomerization of alkenylcyclohexane radicals. Here, we will discuss all the possible pathways of decomposition of the alkenyl radical. Alkenyl radical can undergo either $\beta - C - C$ scission to form small hydrocarbon, or it can isomerize to form cyclopentane/cyclohexane intermediate by ring closing.

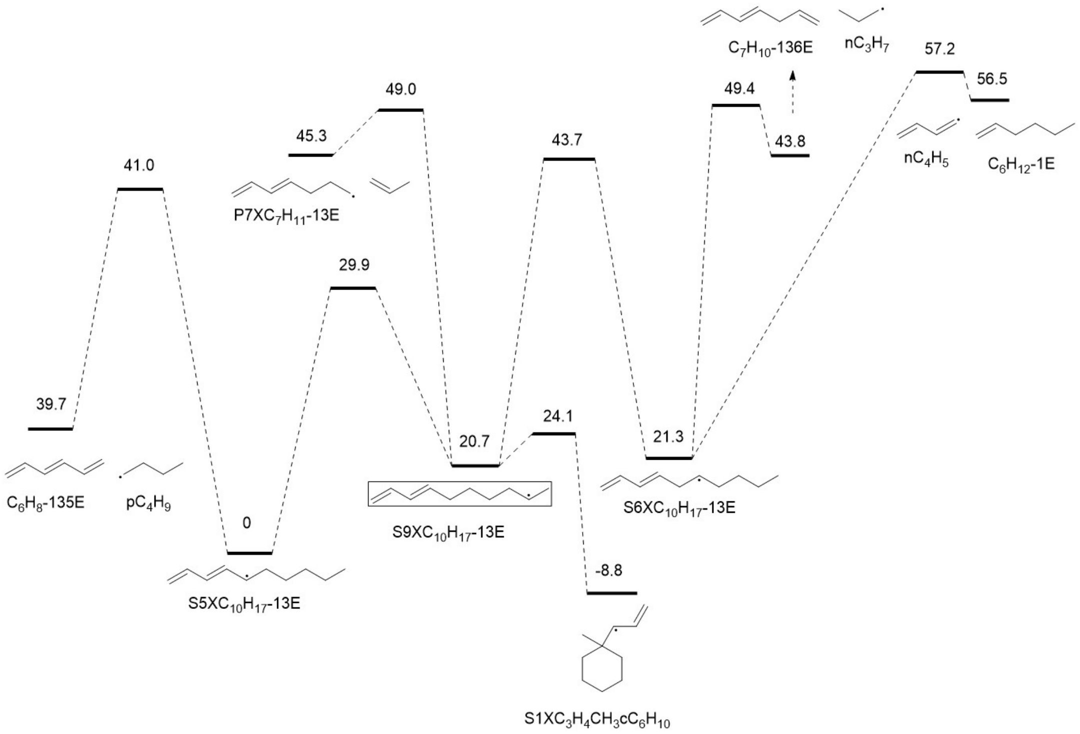

Figure 5.14: Isomerization and decomposition reactions of $S9XC_{10}H_{17} - 13E$.

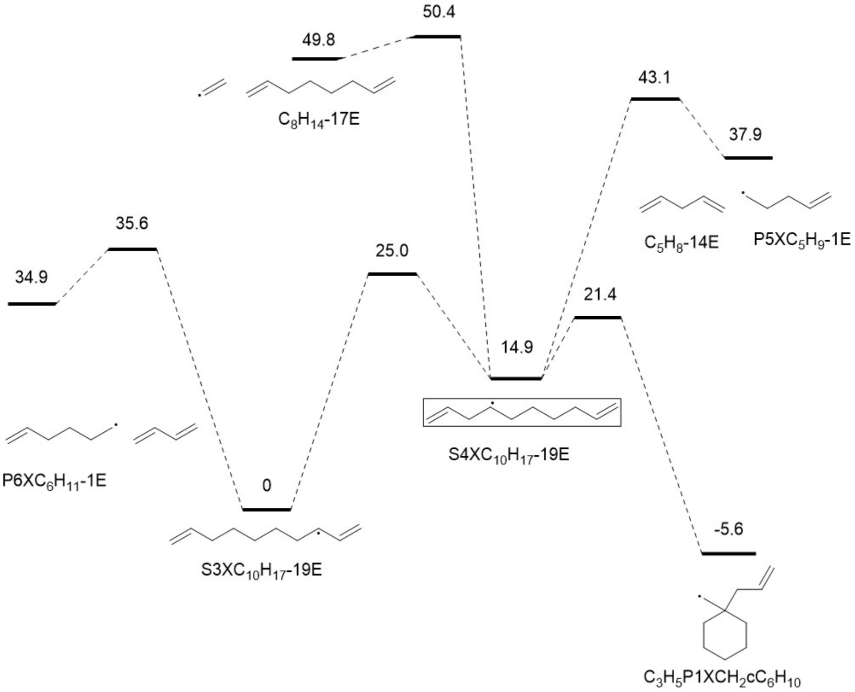

Figure 5.15: Isomerization and decomposition reactions of $S4XC_{10}H_{17}-19E$.

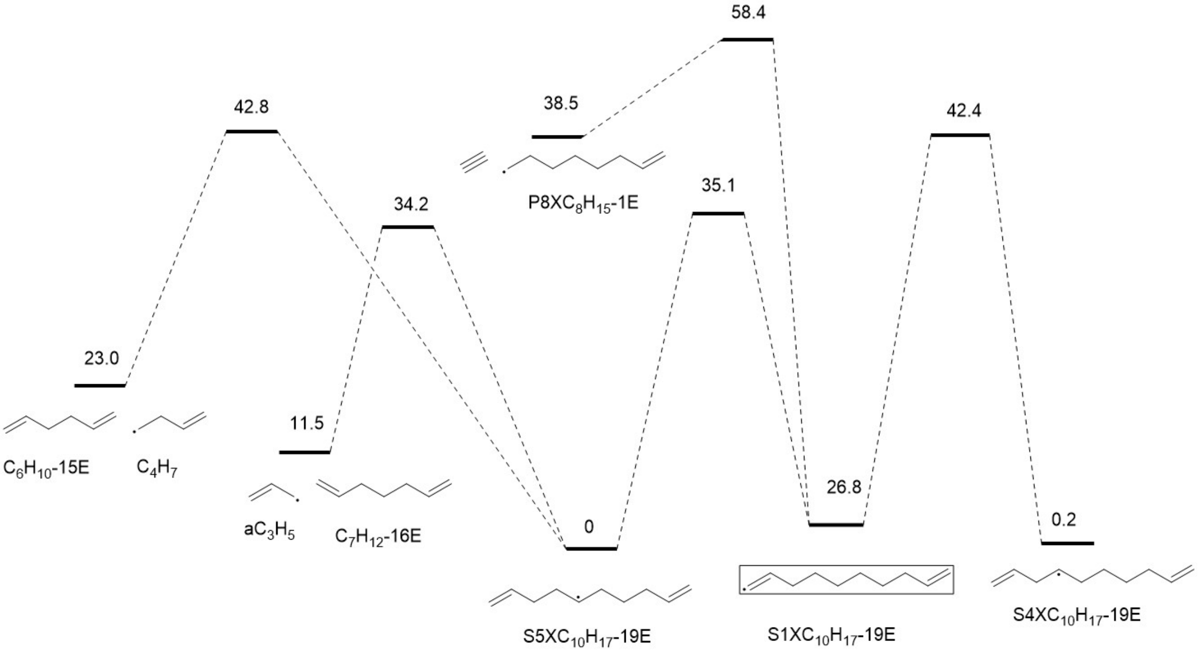

Figure 5.16: Isomerization and decomposition reactions of $S1XC_{10}H_{17}-19E$.

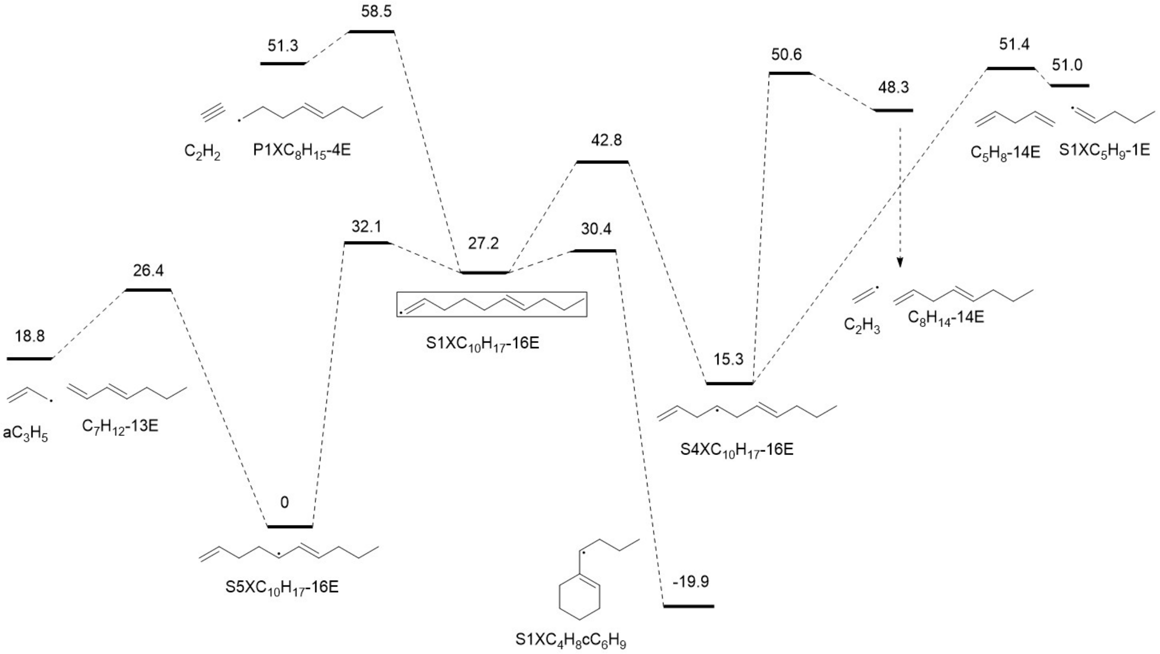

Figure 5.17: Isomerization and decomposition reactions of $S1XC_{10}H_{17}-16E$.

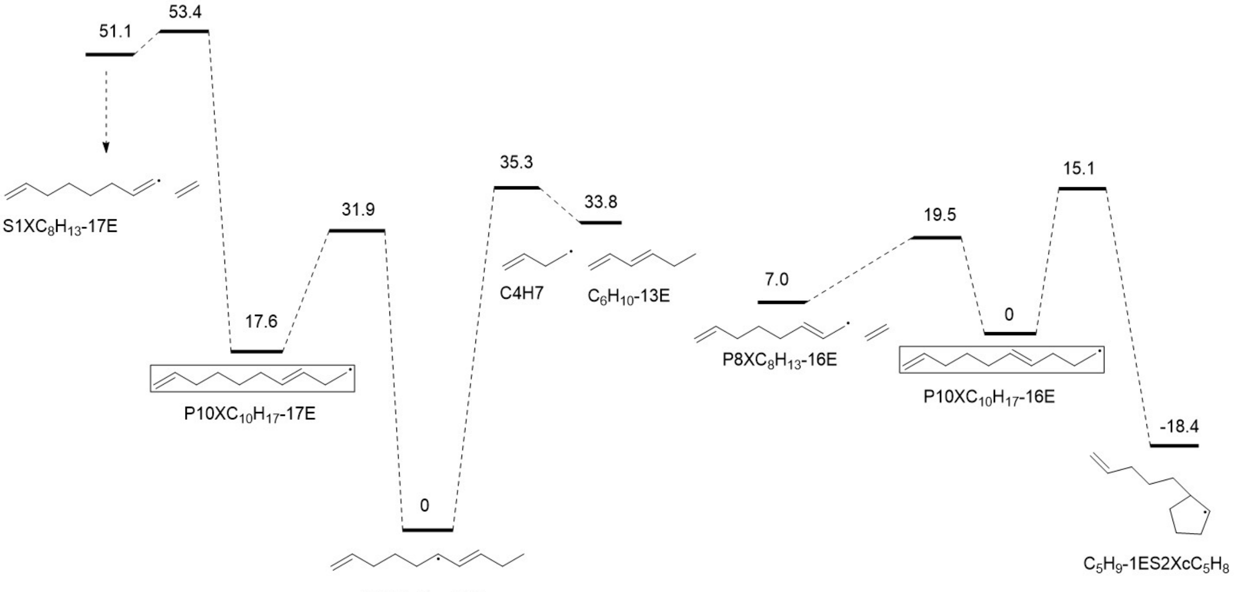

Figure 5.18: Isomerization and decomposition reactions of $P10C_{10}H_{17}-17E$ and $P10XC_{10}H_{17}-16E$.

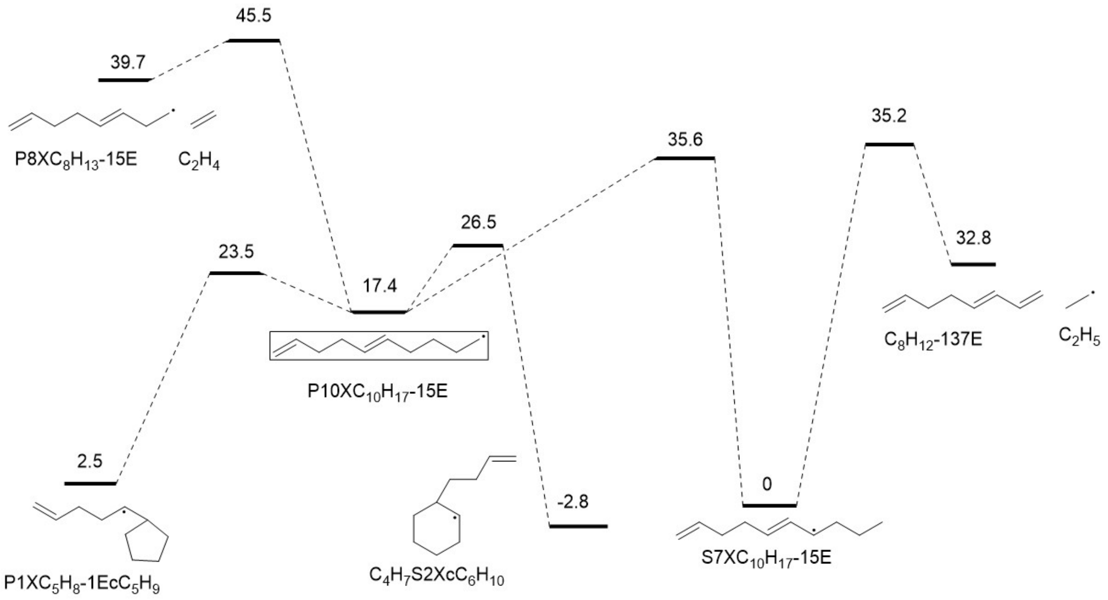

Figure 5.19: Isomerization and decomposition reactions of P10XC10H17-15E.

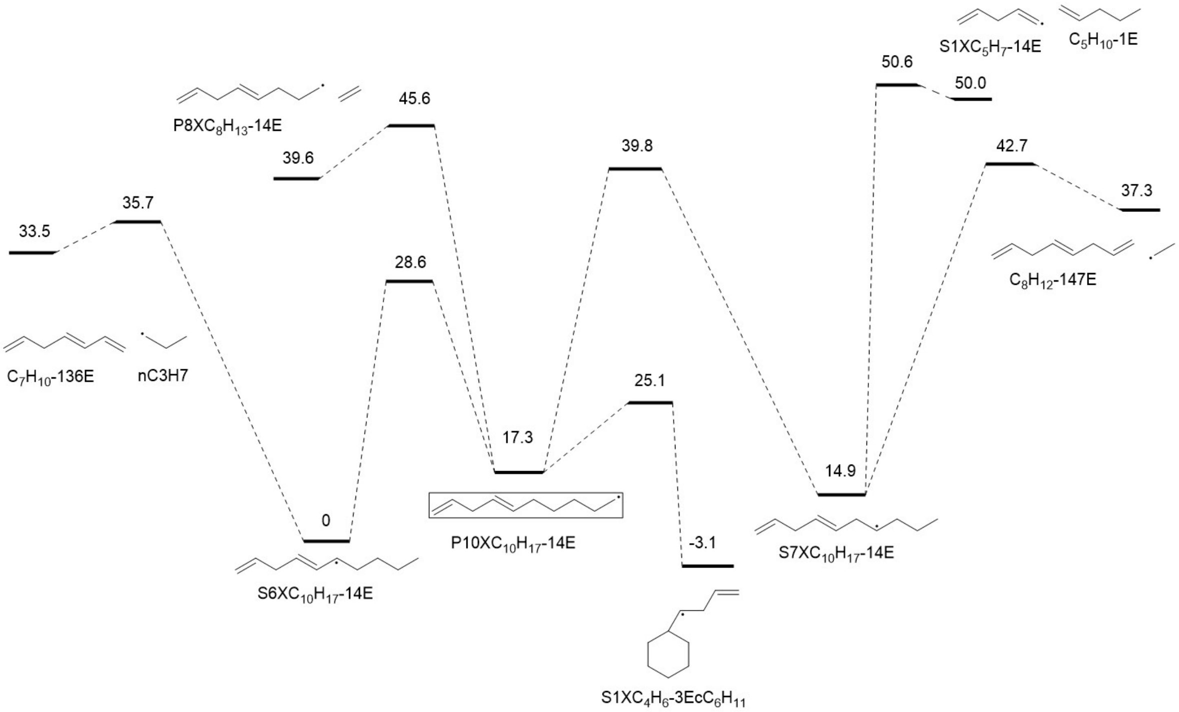

Figure 5.20: Isomerization and decomposition reactions of $P10XC_{10}H_{17} - 14E$.

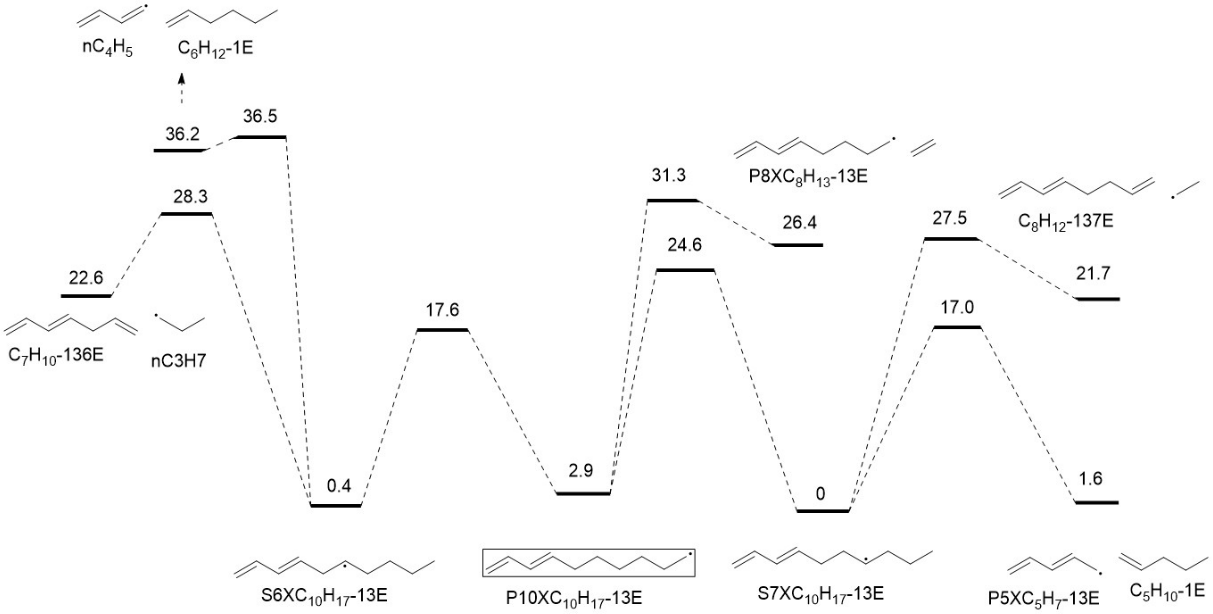

Figure 5.21: Isomerization and decomposition reactions of $P10XC_{10}H_{17} - 13E$.

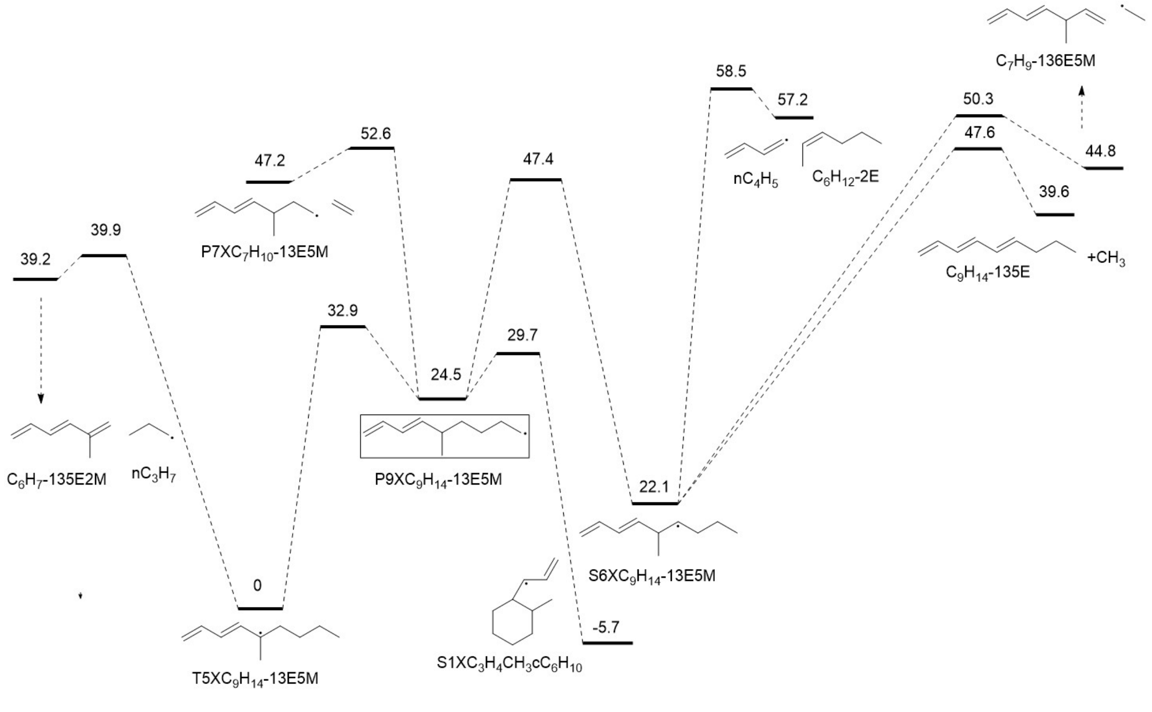

Figure 5.22: Isomerization and decomposition reactions of $P9XC_9H_{14} - 13E5M$.

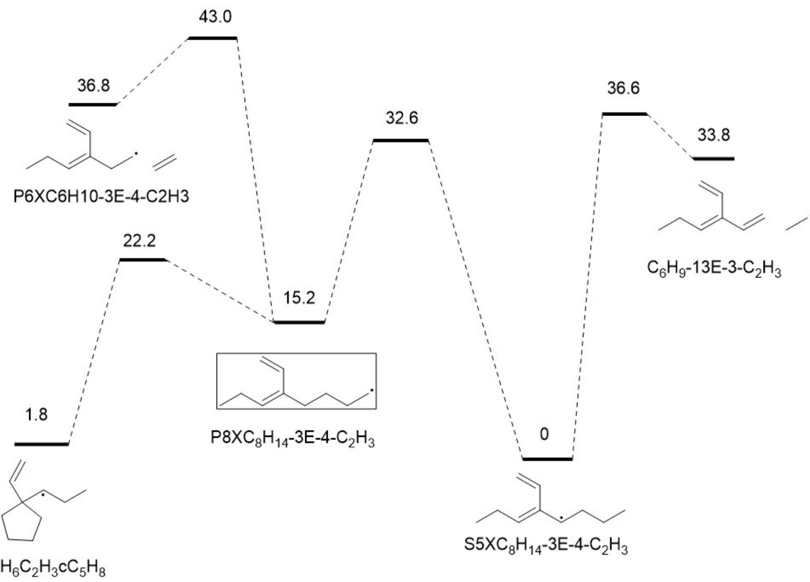

Figure 5.23: Isomerization and decomposition reactions of $P8XC_8H_{14}-3E-4-C_2H_3$.

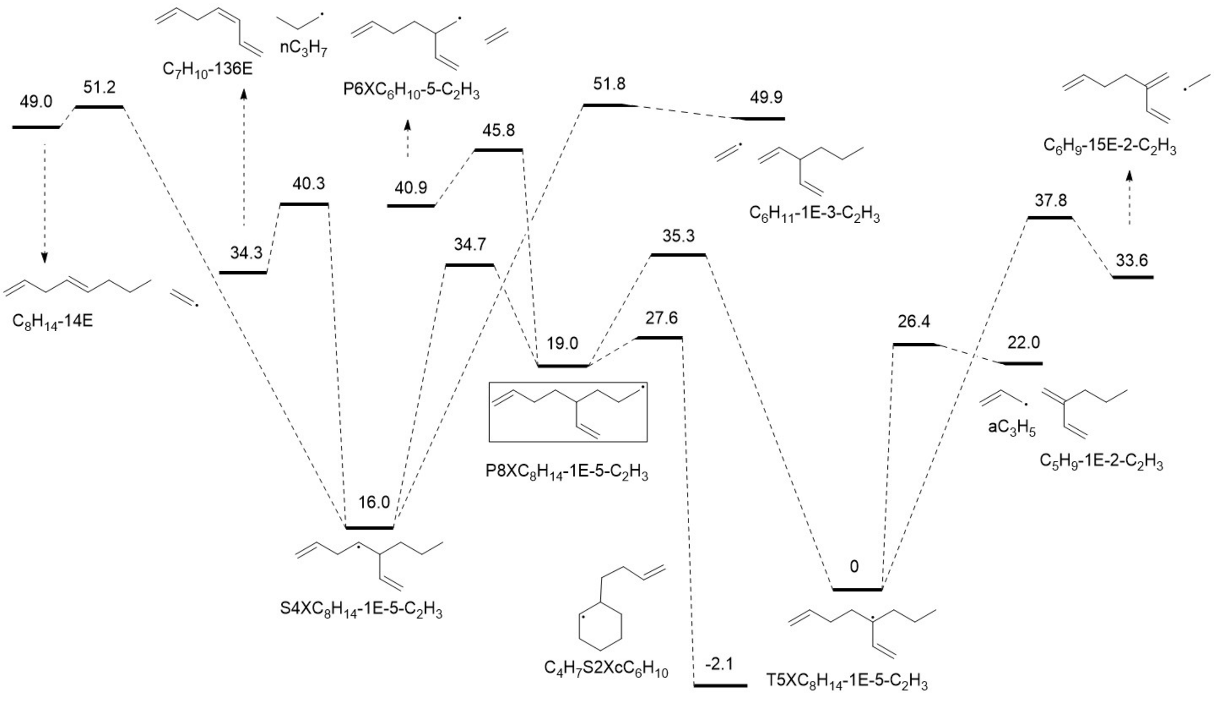

Figure 5.24: Isomerization and decomposition reactions of $P8XC_8H_{14}-1E-5-C_2H_3$.

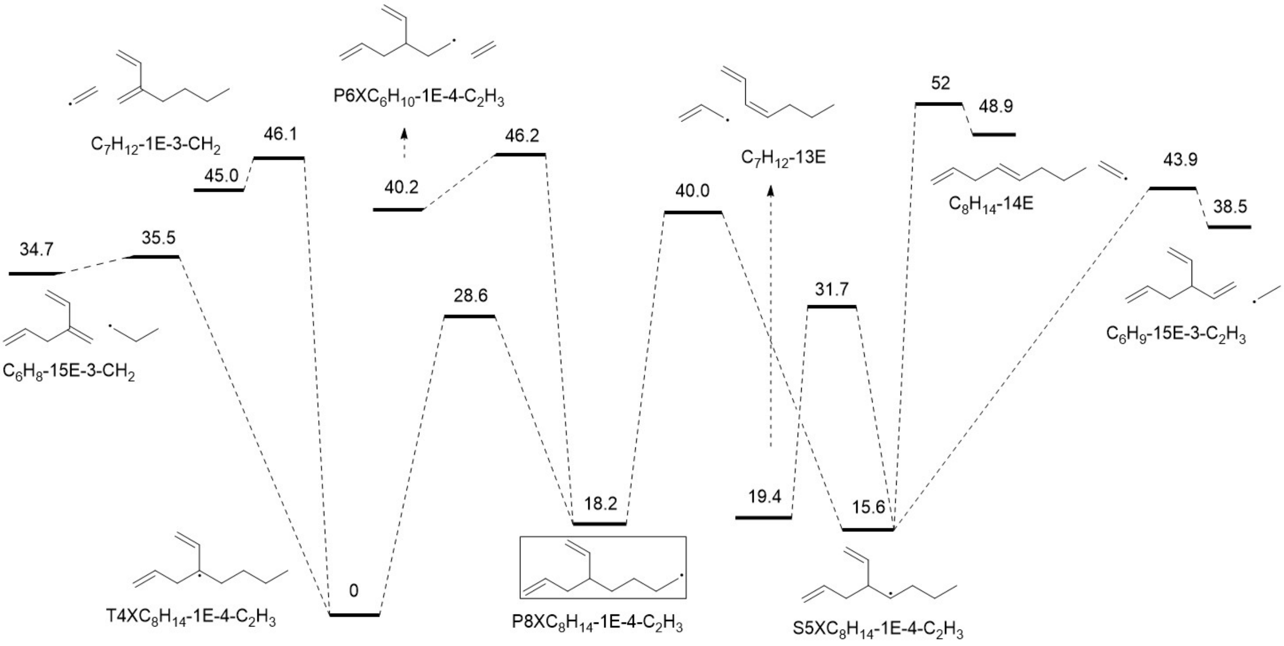

Figure 5.25: Isomerization and decomposition reactions of $P8XC_8H_{14}-1E-4-C_2H_3$.

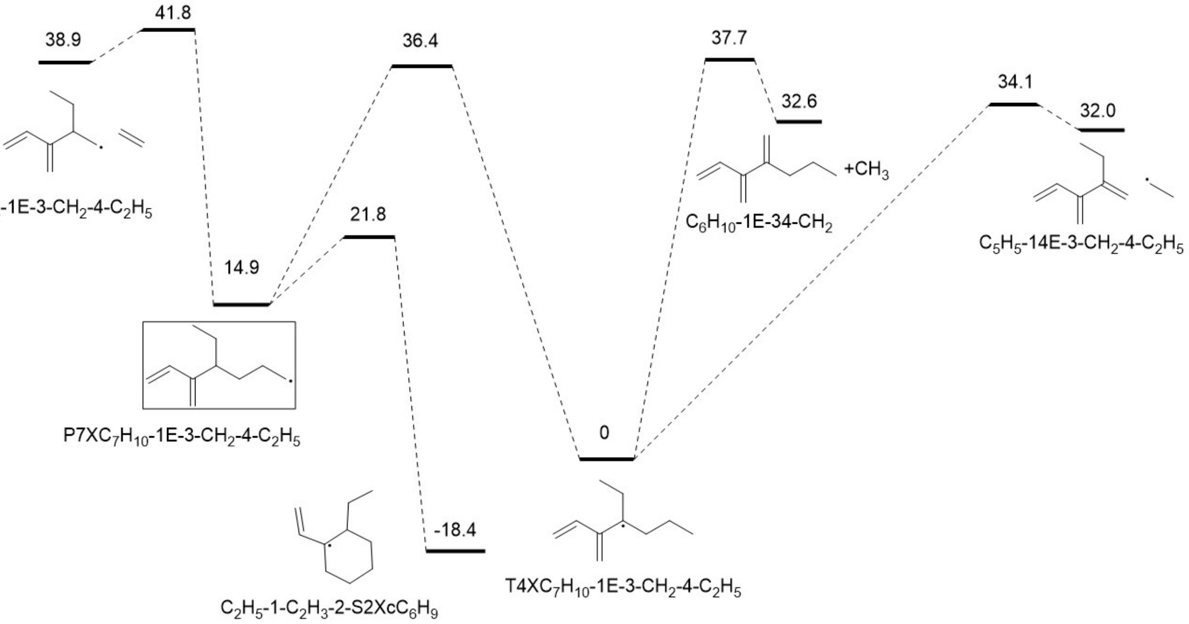

Figure 5.26: Isomerization and decomposition reactions of $P7XC_7H_{10}-1E-3-CH_2-4-C_2H_5$.

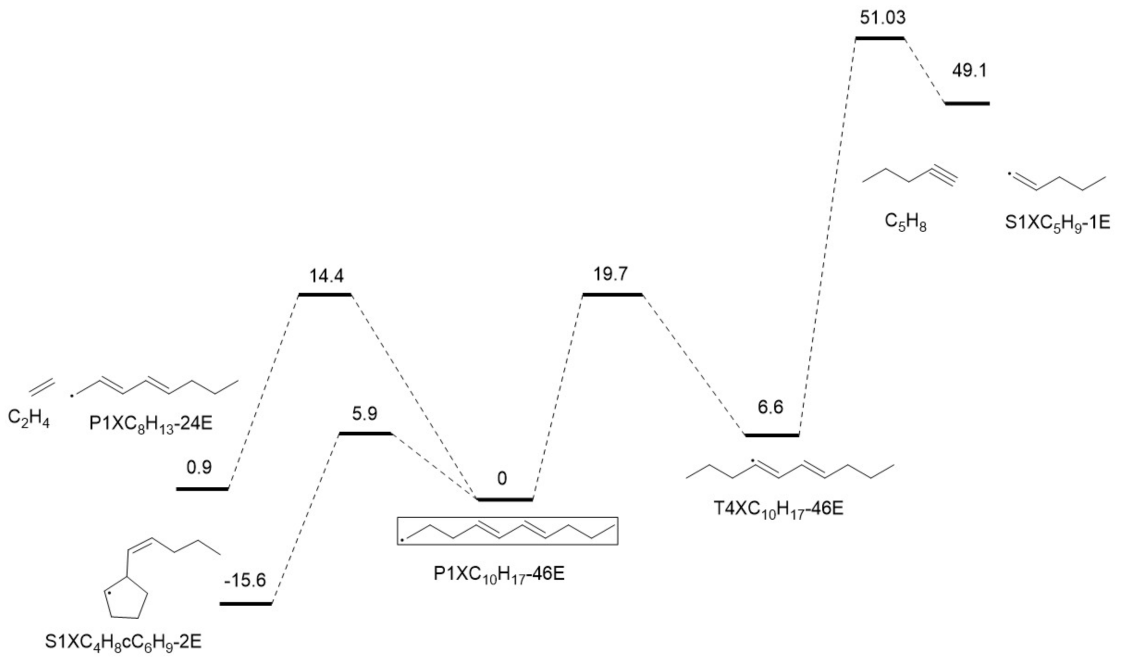

Figure 5.27: Isomerization and decomposition reactions of $P1XC_{10}H_{17} - 46E$.

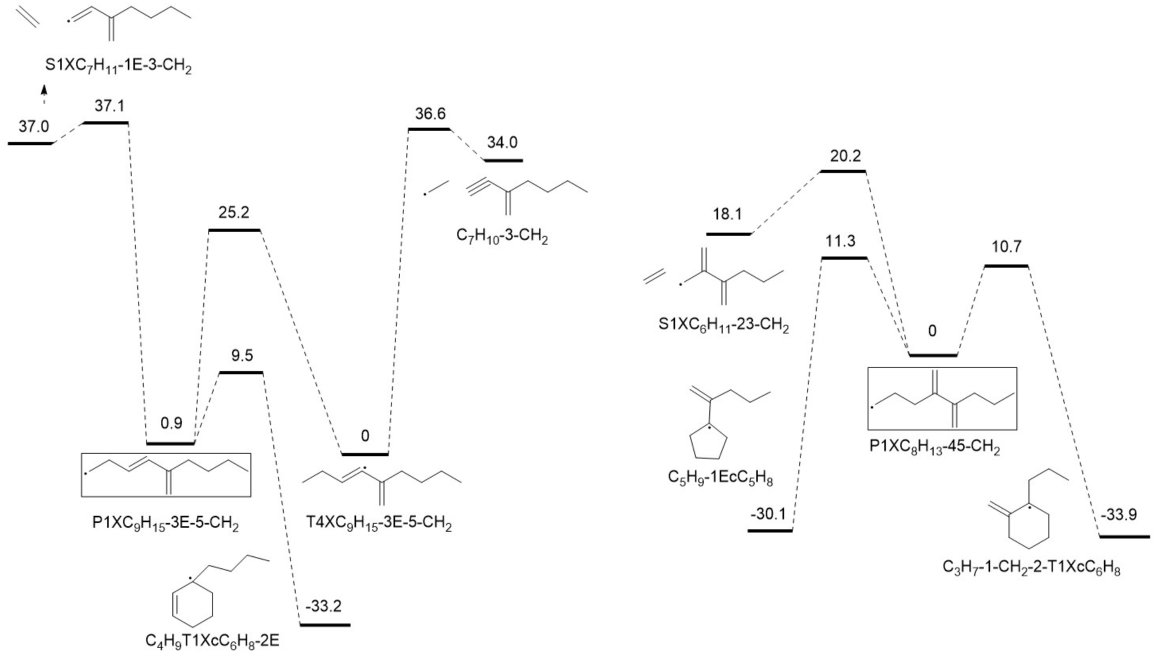

Figure 5.28: Isomerization and decomposition reactions of $P1XC_9H_{15} - 3E - 5 - CH_2$ and $P1XC_8H_{13} - 45 - CH_2$.

It can also isomerize to other alkenyl radicals by intramolecular H-migration. Here also we consider only 1,4-H shift and 1,5-H shift for intramolecular H-migration. We can see from all PES (Figure 5.14, 5.15, 5.16, 5.17, 5.18, 5.19, 5.20, 5.21, 5.22, 5.23, 5.24, 5.25, 5.26, 5.27, and 5.28) that isomerization to cyclopentene/cyclohexane radical is the lowest energy pathways. $\beta - C - C$ scission of all the alkenyl radicals leads to several small hydrocarbons which include triene(hexatriene,heptatriene) diene (butadiene, pentadiene, octadiene etc.), alkene (ethylene, propene, butene,hexene ect.), alkyl-radical (CH_3, C_2H_5, pC_4H_9 etc.) etc.

5.3.1.6 Dissociation of alkenecyclohexane

From the isomerization of decalin, three different alkenecyclohexane can be formed and these can further undergo decomposition. In this work, we have considered both H-abstraction and C-C dissociation reactions. Liu et al.[18] studied C4-C6 alkenes theoretically and showed that allylic H-abstraction is the most energetically favourable. Hence, we have considered only the allylic H-abstraction reactions in the present study. Also,Wang's[19] theoretical study also showed that the allylic C-C bond has the lowest dissociation energy. Hence, we have considered only the allylic C-C bond dissociation in this work. Figure 5.29 shows the PES.

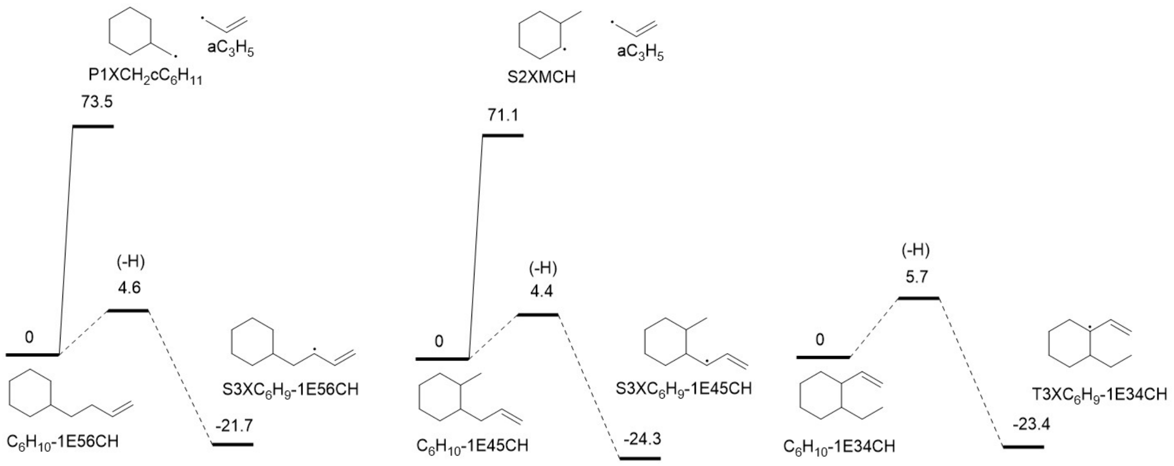

Figure 5.29: H-abstraction and decomposition reactions of $C_6H_{10} - 1E56CH$, $C_6H_{10} - 1E45CH$, and $C_6H_{10} - 1E34CH$. (-H) indicates H-abstraction reaction by H atom. The solid line indicates reaction without saddle point. Energy unit: kcal/mol.

5.3.1.7 Stepwise dehydrogenation of cyclic intermediate

From the isomerization of the alkenyl radical, cyclopentane radicals and cyclohexane radicals are formed. From the isomerization of alkenylcyclohexane radical, methylhydrindane radicals and cyclohexane radicals are formed. From the H-elimination from decalin radicals, olefinic decalin intermediate is formed.

Methylhydrindane radicals

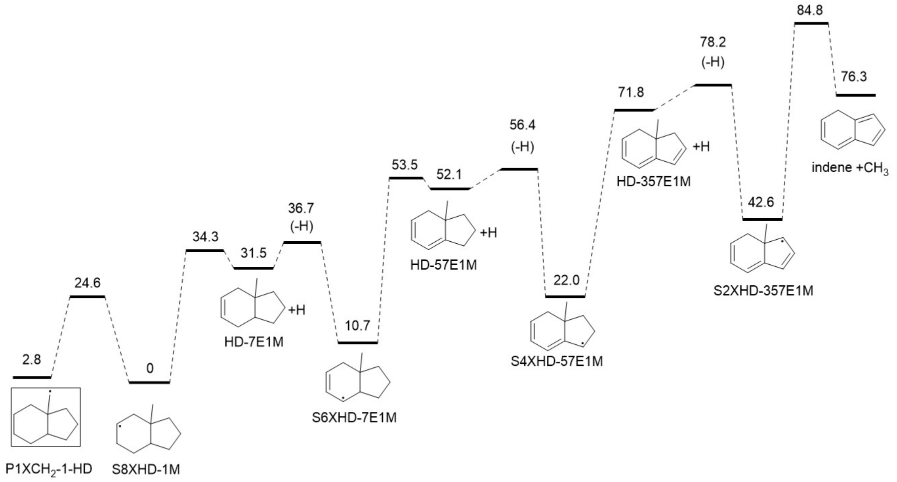

Figure 5.30: Isomerization and decomposition reactions of $P1XCH_2 - 1 - HD$.

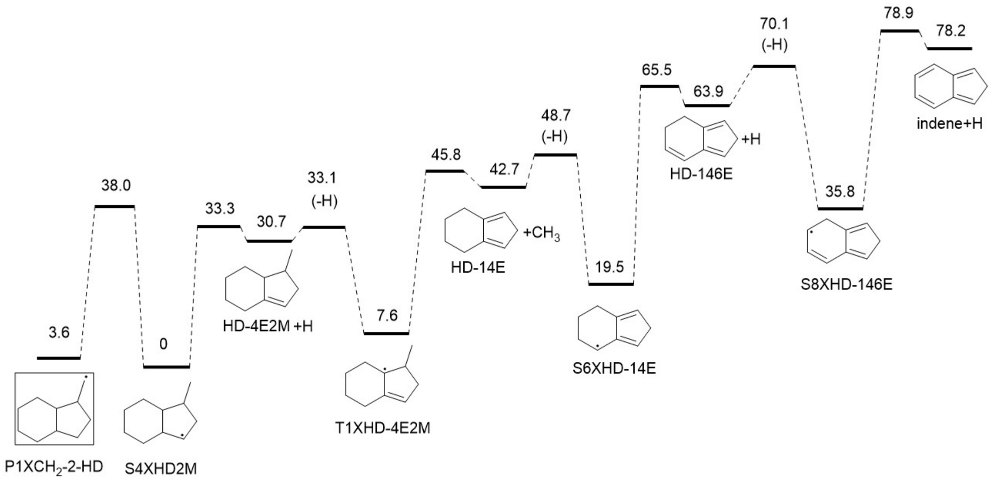

Figure 5.31: Isomerization and decomposition reactions of $P1XCH_2 - 2 - HD$.

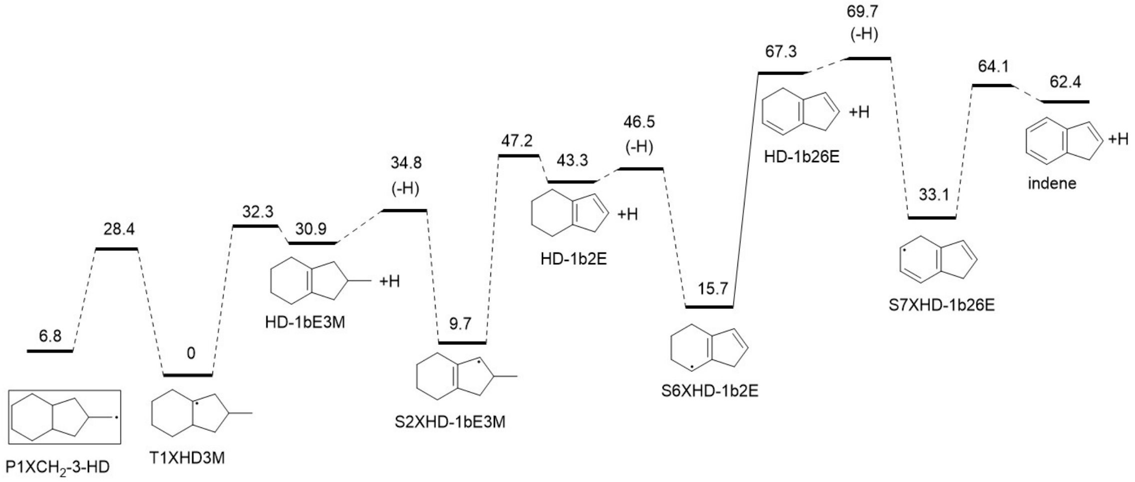

Figure 5.32: Isomerization and decomposition reactions of $P1XCH_2-3-HD$.

Figures 5.30, 5.31 and 5.32 show the stepwise dehydrogenation of three methylhydrindane radicals. All these radical form indene by stepwise dehydrogenetion.

Olefinic decalin intermediate

Figures 5.33, 5.34 and 5.35 show PES of stepwise dehydrogenation and decomposition of olefinic decalin intermediates.

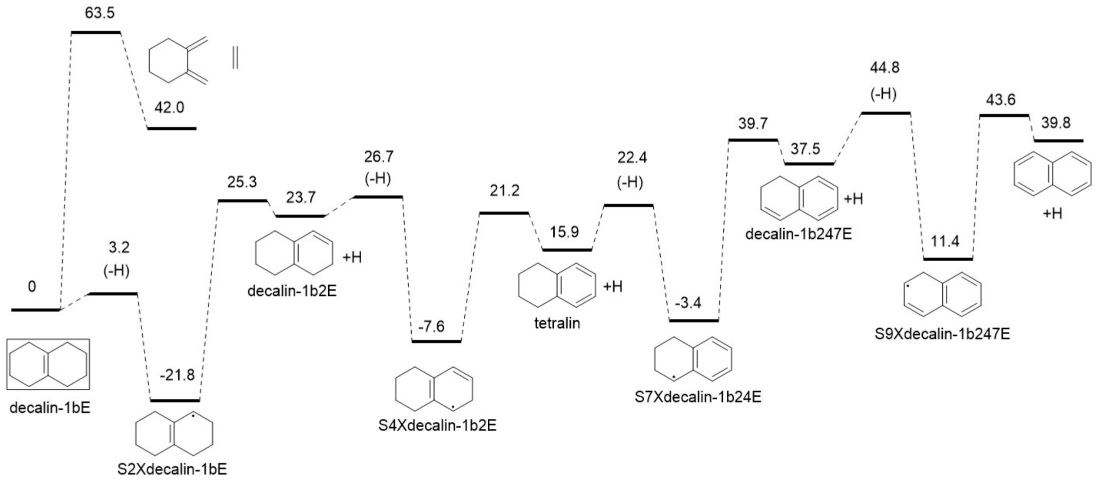

Figure 5.33: Stepwise dehydrogenation and decomposition reactions of decalin-1bE.

Olefinic decalin intermediates can dissociate by reverse DA reaction. Decalin-1bE has lowest energy barrier for reverce DA reaction. Stepwise dehydrogenation

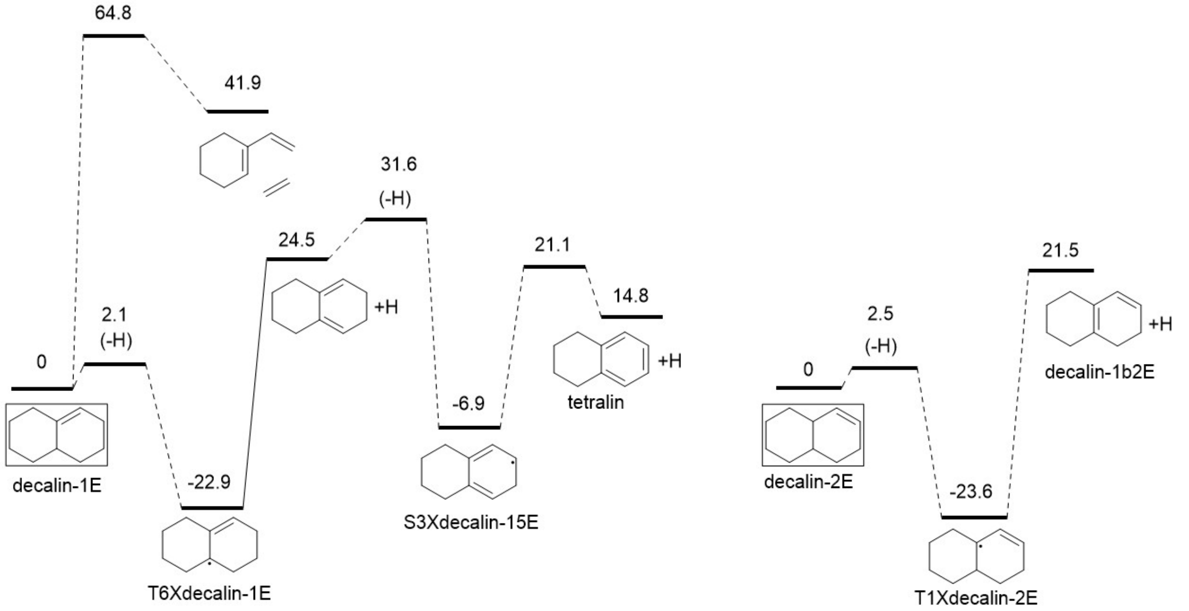

Figure 5.34: Stepwize dehydrogenation and decomposition reactions of decalin-1E and decalin-2E.

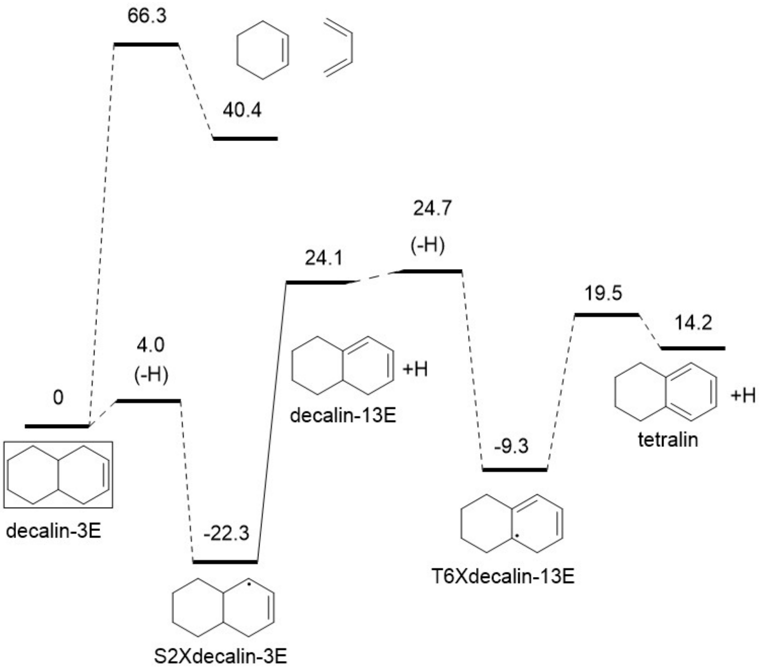

Figure 5.35: Stepwize dehydrogenation and decomposition reactions of decalin-3E.

of olefinic decalin intermediates leads to tetralin and naphthalene.

Cyclohexane radical

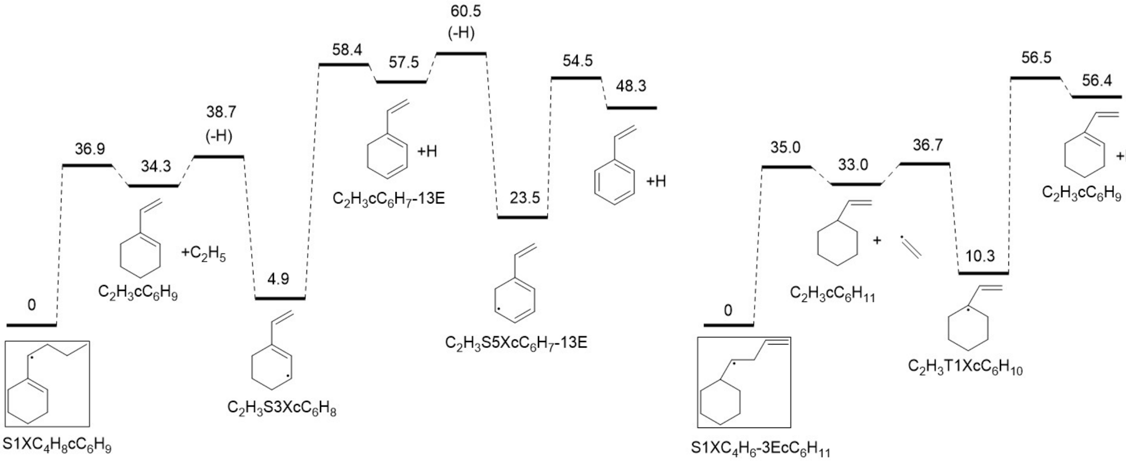

Figure 5.36: Stepwise dehydrogenation and decomposition reactions of $S1XC_4H_8cC_6H_9$ and $S1XC_4H_6-3EcC_6H_{11}$.

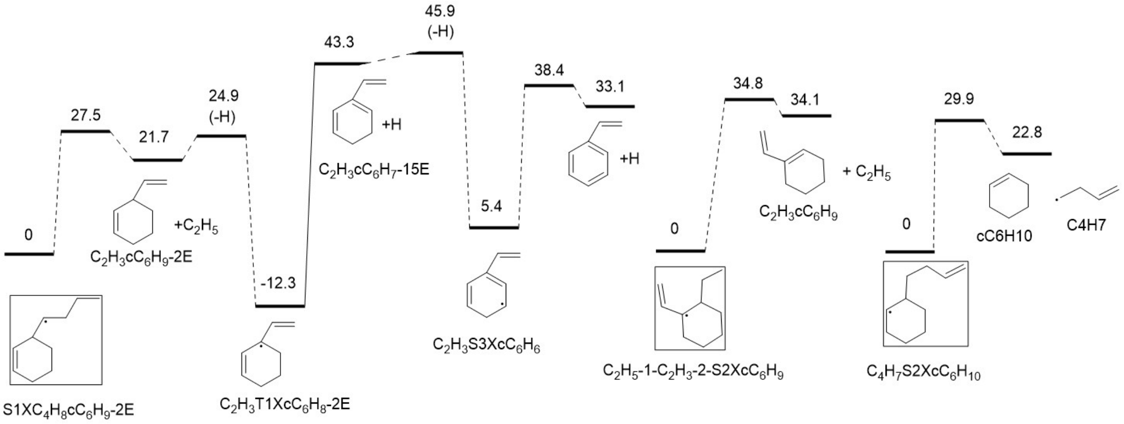

Figure 5.37: Stepwise dehydrogenation and decomposition reactions of $S1XC_4H_8cC_6H_9 - 2E$, $C_2H_5 - 1 - C_2H_3 - 2 - S2XcC_6H_9$ and $C_4H_7S2XC_6H_{10}$.

Figures 5.36, 5.37, 5.38 5.39, and 5.40 show PES of stepwise dehydrogenation and decomposition of cyclohexane radicals. Suscesive dehydrogenation of these cyclohexane radicals are source of the formation of many aromatics. Stepwise dehydrogenation of $S1XC_4H_8cC_6H_9$, $S1XC_4H_6 - 3EcC_6H_{11}$, $S1XC_4H_8cC_6H_9 - 2E$ and $C_2H_5 - 1 - C_2H_3 - 2 - S2XcC_6H_9$ (figure 5.36 and 5.37) leads to styrene.

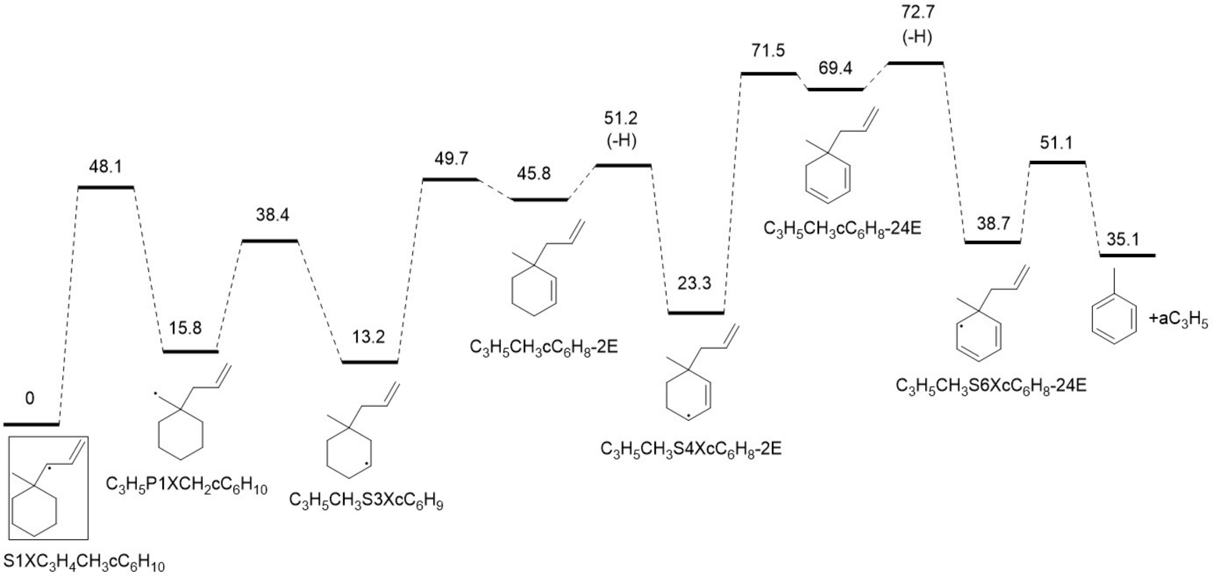

Figure 5.38: Stepwise dehydrogenation and decomposition reactions of $S1XC_4H_8cC_6H_9 - 2E$.

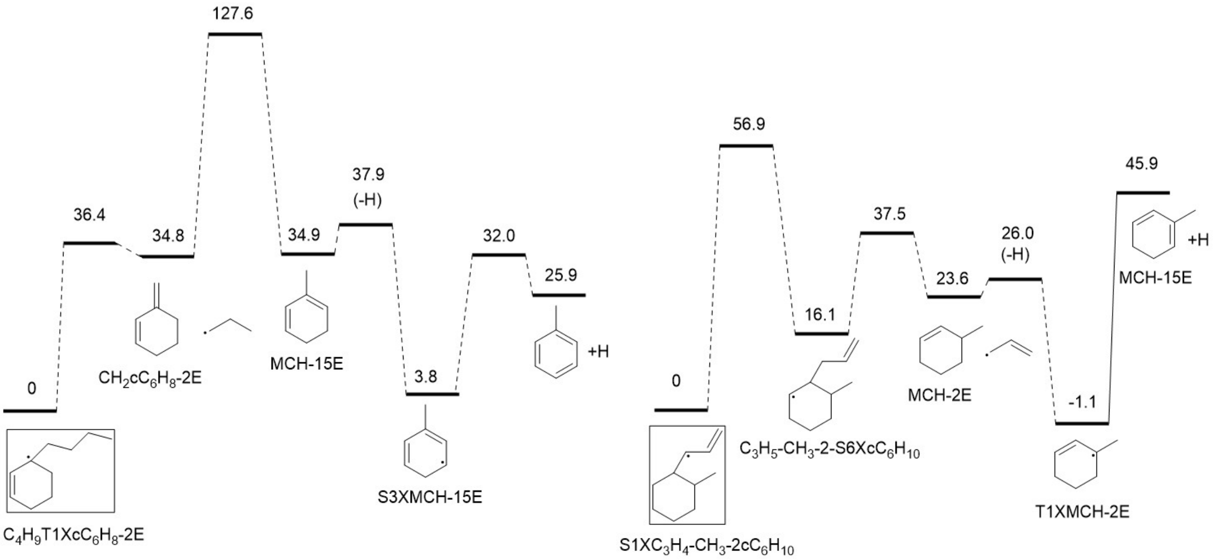

Figure 5.39: Stepwise dehydrogenation and decomposition reactions of $C_4H_9T1XcC_6H_8 - 2E$ and $S1XC_3H_4 - CH_3 - 2cC_6H_{10}$.

$C_4H_7S2XC_6H_{10}$ (figure 5.37) leads to cyclohexene, which can form benzene by stepwise dehydrogenation. $S1XC_4H_8cC_6H_9 - 2E$, $C_4H_9T1XcC_6H_8 - 2E$ and $S1XC_3H_4 - CH_3 - 2cC_6H_{10}$ (figure 5.38 and 5.39) leads to toluene. $C_3H_7 - 1 -$

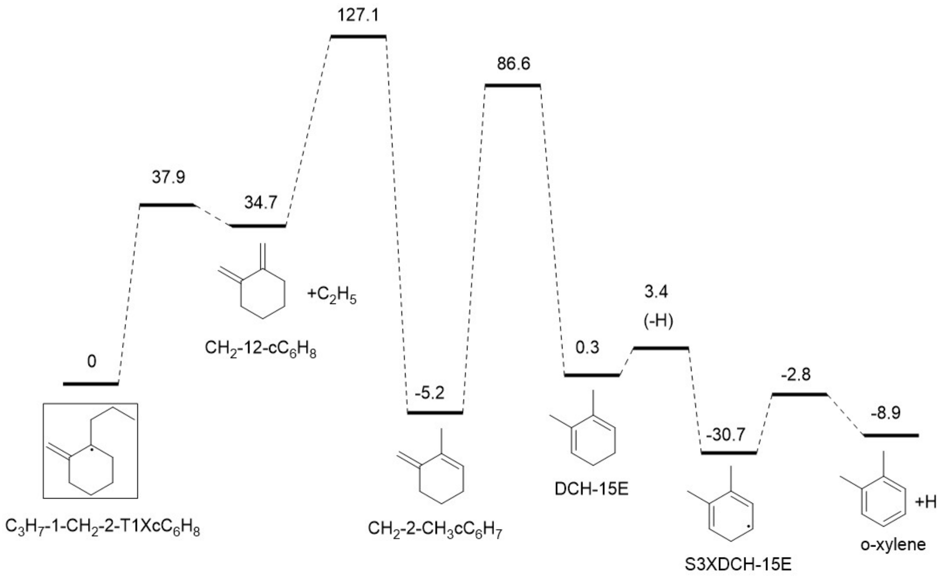

Figure 5.40: Stepwise dehydrogenation and decomposition reactions of $C_3H_7-1-CH_2-2-T1XcC_6H_8$.

$CH_2-2-T1XcC_6H_8$ (figure 5.40) leads to o-xylene.

Cyclopentane radical

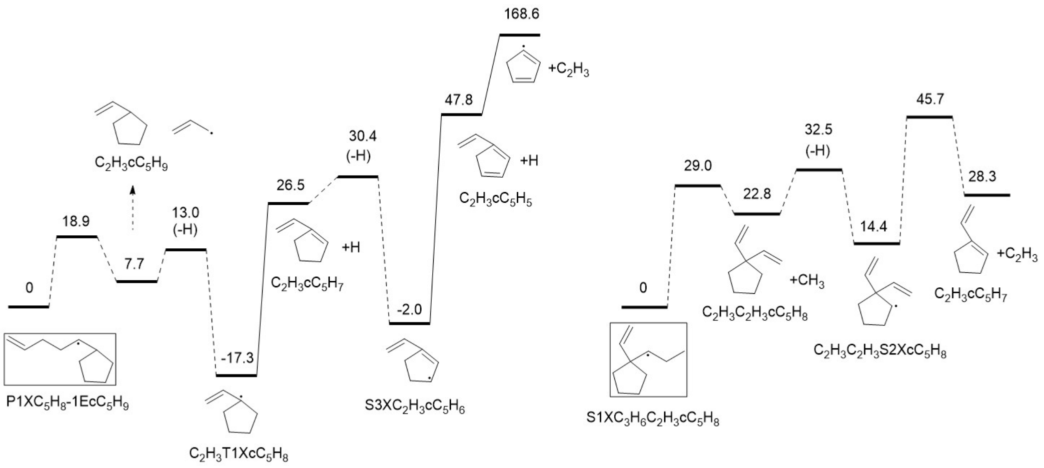

Figure 5.41: Stepwise dehydrogenation and decomposition reactions of $P1XC_5H_8-1EcC_5H_9$ and $S1XC_3H_6C_2H_3cC_5H_8$.

Figures 5.41 and 5.42 show PES of stepwise dehydrogenation and decomposition of cyclopantane radicals. Stepwise dehydrogenation and decomposition of

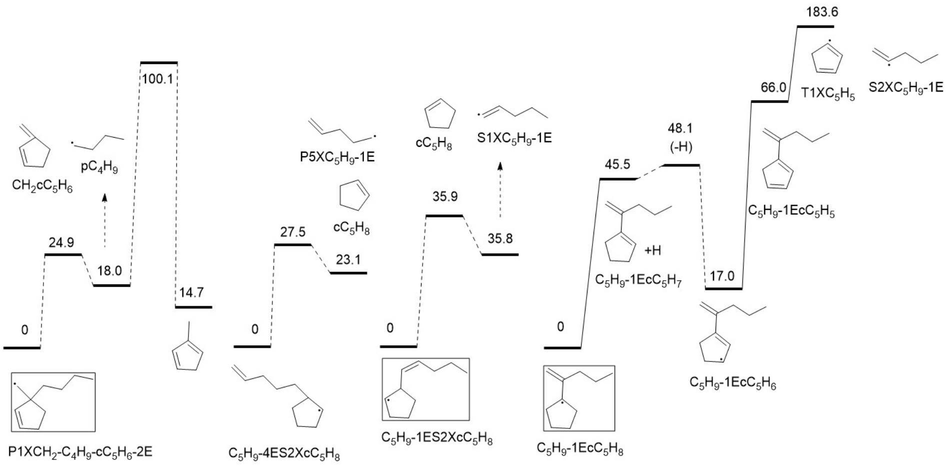

Figure 5.42: Stepwise dehydrogenation and decomposition reactions of $P1XCH_2-C_4H_9-cC_5H_6-2E$, $C_5H_9-1ES2XcC_5H_8$ and $C_5H_9-1EcC_5H_8$.

these radicals lead to cyclopentene, cyclopentadiene and methylcyclopentadiene.

5.3.2 Rate Calculation

We calculate the high-pressure limit (HPL) rate for all the reactions using TST for the reaction with saddle point and VTST for the reaction without saddle point for the temperature range of 800-2000K.

5.3.2.1 Unimolecular decomposition and isomerization of decalin

Unimolecular decomposition channel (i.e., $C-H$ dissociation channel) is not associated with any saddle point. As such, we did stepwise optimization (relax scan, figure 5.43) to get PES and then calculate rate parameters using VTST. Isomerization of decalin occurs through two steps (Figure 5.2), and we have calculated rate parameters for both steps. From figure 5.3, we can see that at MRCI method, in one of the cases, energy of TS of H-migration step (2nd step of isomerization process) is less than biradical intermediate (biradical2 to $C_6H_{10}-1E56CH$). This was encountered for the isomerization process of methyl-cyclohexane as well. In that study, the authors artificially increased the energy of the corresponding TS[16]. In our study, we did not want to follow this artificial procedure and we used CASSCF energy barriers for 2nd step of the isomerization process. As figure 5.43 shows, the barrier height of the variational transition state varies from 69.7 to 80.6 kcal/mol with C-H bond stretching 2.5 to 3.3 Å within the studied temperature range. Figure 5.44 shows the rate of C-H dissociation and ring-opening isomerization. From the figure we can see that ring-opening isomerization process is much faster than

C-H dissociation channels. C1-C2 bond dissociation leading to birabical1 is the fastest process among them.

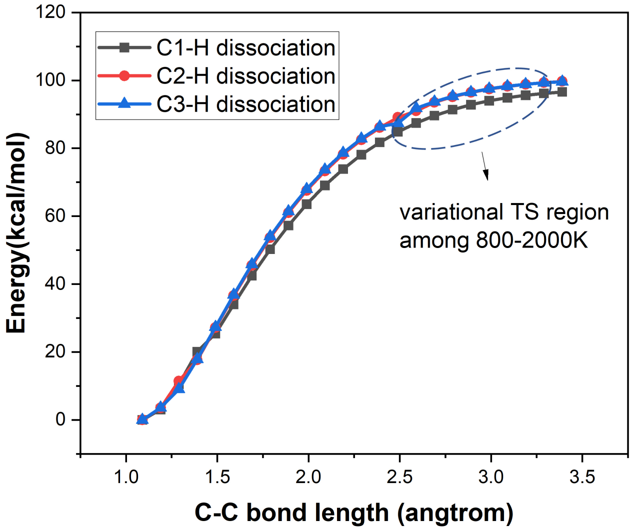

Figure 5.43: Stepwise optimized potential energy curve of $C-H$ dissociation. Method: MRCI/6-31+g(d,p)//CAS(2,2)/ 6-31+g(d,p).

Among C-H dissociation channels, C3-H dissociation is faster.

From figures 5.44 and 5.45, we can see that for all isomerization reactions, the rate constant of the ring-opening step (1st step) to form biradical is much less than the H-migration step (2nd step). H-migration from biradical3 is much faster than H-migration from other two biradicals.

5.3.2.2 H-abstraction reaction by H atom and CH_3 radical

Figure 5.46 and figure 5.47 show the Arrhenius plot for rate constant of H-abstraction reaction. Rate constant of H-abstraction from decalin by H atom is higher than the rate constant of H-abstraction from decalin by CH_3 radical. In both cases, rate constant for H-atom abstraction at the tertiary carbon is the lowest.

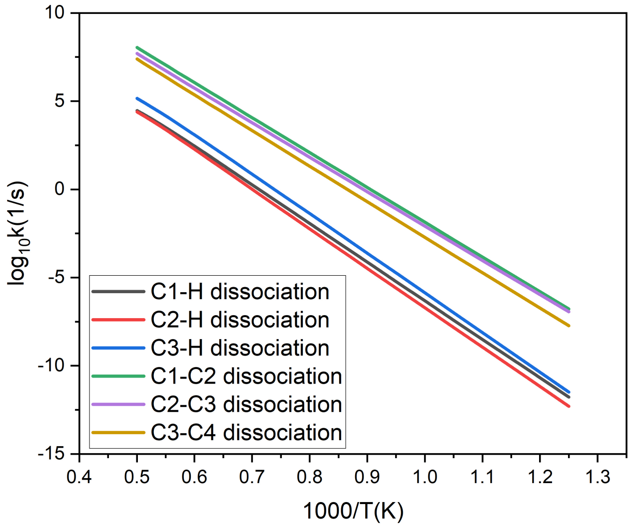

Figure 5.44: HPL rate constant for decalin decomposition and ring-opening step of isomerization, i.e., first step to form biradical.

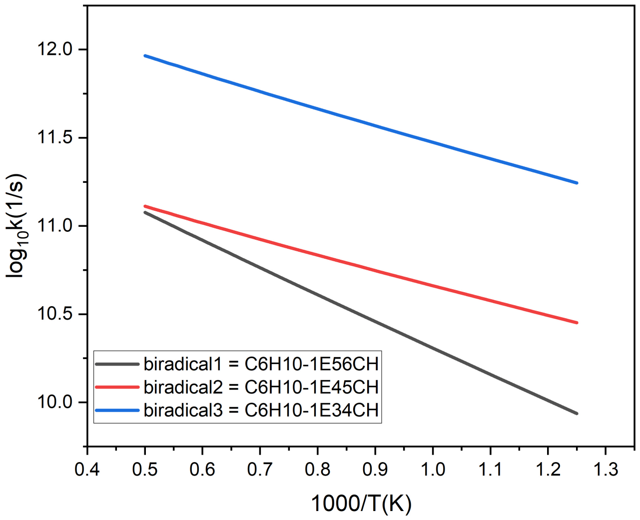

Figure 5.45: HPL rate constant for 2nd step of isomerization of decalin i.e., intramolecular H-migration from biradical to form alkene.

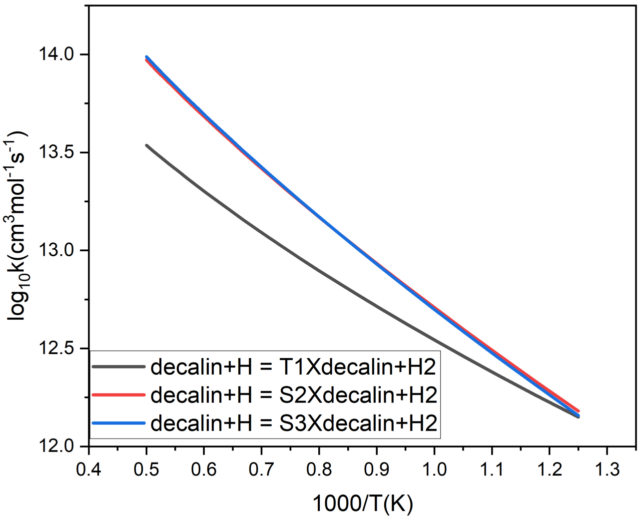

Figure 5.46: Rate constant of H-atom abstraction of decalin from H atom.

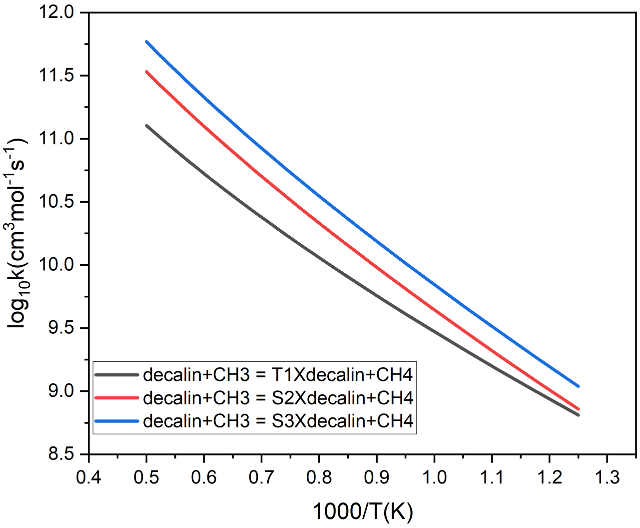

Figure 5.47: Rate constant of H-atom abstraction of decalin from CH_3 radical.

5.3.3 Kinetic parameters

Kinetic parameters A, and E_a for all the reactions were obtained by fitting the calculated rate constant over the temperature range of 800-2000 K. All the kinetic parameters are listed in table 5.5.

Table 5.5: High pressure limit rate parameter of decalin decomposition reactions.

No	**Reaction**	**A**	E_a
Unimolecular decomposition and isomerization of decalin			
1	decalin = S2Xdecalin+H	4.65E+15	102378.6
2	decalin = S3Xdecalin+H	2.84E+16	102114.3
3	decalin = T1Xdecalin+H	3.13E+15	99757.4
4	decalin = biradical1	8.21E+17	90485.2
5	decalin = biradical2	2.92E+17	89428.0
6	decalin = biradical3	2.92E+17	92329.3
7	$biradical1 = C_6H_{10} - 1E56CH$	2.92E+17	92329.3
8	$biradical2 = C_6H_{10} - 1E45CH$	3.52E+11	4045.3
9	$biradical3 = C_6H_{10} - 1E34CH$	2.76E+12	4419.7
abstraction reaction by H atom and CH_3 radical			
10	$decalin + H = S2Xdecalin + H_2$	1.34E+15	11023.2
11	$decalin + H = S3Xdecalin + H_2$	1.48E+15	11258.3
12	$decalin + H = T1Xdecalin + H_2$	2.66E+14	8556.9
13	$decalin + CH3 = S2Xdecalin + CH_4$	1.80E+13	16449.0
14	$decalin + CH3 = S3Xdecalin + CH_4$	3.40E+13	16798.8
15	$decalin + CH3 = T1Xdecalin + CH_4$	3.78E+12	14134.4
decomposition and isomerization of decalin radicals			
16	T1Xdecalin = decalin-1bE+H	2.81E+14	35378.1
17	T1Xdecalin = decalin-1E+H	3.94E+14	37802.5
18	S2Xdecalin = decalin-1E+H	6.30E+13	36745.3
19	S2Xdecalin = decalin-2E+H	2.21E+14	38132.4
20	S3Xdecalin = decalin-2E+H	2.27E+14	38364.9
21	S3Xdecalin = decalin-3E+H	2.85E+14	37991.3

No	Reaction	A	E_a
22	$T1Xdecalin = P6XC_6H_9 - 1E23CH$	3.60E+14	36165.1
23	$T1Xdecalin = P6XC_6H_9 - 1E12CH$	1.81E+14	32888.2
24	$S3Xdecalin = S6XC_6H_{10} - 1E56CH$	6.68E+13	31715.7
25	$S3Xdecalin = P6XC_6H_9 - 1E45CH$	1.07E+14	32631.8
26	$S2Xdecalin = S6XcC_{10}H_{17} - 1E$	5.16E+13	30459.8
27	$S2Xdecalin = P4XC_4H_8cC_6H_9$	1.97E+14	37252.1
28	$S2Xdecalin = P6XC_6H_9 - 1E34CH$	9.66E+13	31735.6
decomposition and isomerization of alkenyl-cyclohexane radicals			
29	$P4XC_4H_8cC_6H_9 = TXC_4H_8cC_6H_8$	3.75E+11	10156.4
30	$P4XC_4H_8cC_6H_9 = S1XC_4H_8cC_6H_9$	1.60E+12	13057.7
31	$P4XC_4H_8cC_6H_9 = PXC_2H_4cC_6H_9 - 2E + C_2H_4$	1.99E+14	29847.7
32	$S1XC_4H_8cC_6H_9 = C_2H_3cC_6H_9 + C_2H_5$	3.72E+13	35986.2
33	$TXC_4H_9cC_6H_8 = CH_2cC_6H_8 + nC_3H_7$	8.62E+14	38609.3
34	$TXC_4H_9cC_6H_8 = nC_4H_9cC_6H_7 + H$	3.51E+03	2471.9
35	$S1XC_4H_8cC_6H_9 = P1XC_{10}H_{17} - 46E$	1.30E+13	28456.7
36	$S1XC_4H_8cC_6H_9 = S1XC_{10}H_{17} - 16E$	3.12E+13	53743.8
37	$TXC_4H_9cC_6H_8 = P1XC_9H_{15} - 3E - 5 - CH_2$	1.08E+14	44030.4
38	$P6XC_6H_9 - 1E12CH = S1XC_6H_9 - 1E12CH$	9.77E+11	18147.9
39	$S1XC_6H_9 - 1E12CH = C_2H_3cC_6H_9 + C_2H_5$	2.96E+14	36477.0
40	$P6XC_6H_9 - 1E12CH = PXC_2H_4cC_6H_9 + C_2H_4$	2.40E+14	16823.8
41	$P6XC_6H_9 - 1E12CH = S1Xspiro - 4 - 5 - DN$	1.36E+11	9447.5
42	$P6XC_6H_9 - 1E23CH = T3XC_6H_9 - 1E23CH$	7.27E+13	19351.8
43	$P6XC_6H_9 - 1E23CH = PXCH_2CH_2cC_6H_9 + C_2H_4$	8.05E+15	32770.9
44	$T3XC_6H_9 - 1E23CH = CH_2 - 12 - cC_6H_8 + C_2H_5$	2.56E+16	43446.2
45	$T3XC_6H_9 - 1E23CH = P1XC_8H_{13} - 45 - CH_2$	5.02E+15	47617.3
46	$P6XC_6H_9 - 1E23CH = P1XCH_2 - 1 - HD$	1.27E+13	15556.6
47	$P6XC_6H_9 - 1E34CH = T3XC_6H_9 - 1E34CH$	6.56E+11	22717.7
48	$P6XC_6H_9 - 1E34CH = C_2H_3S2XcC_6H_{10} + C_2H_4$	1.43E+14	28603.8
49	$T3XC_6H_9 - 1E34CH = C_2H_3cC_6H_9 + C_2H_5$	7.96E+14	37377.2
50	$T3XC_6H_9 - 1E34CH = P8XC_8H_{14} - 3E - 4 - C_2H_3$	3.98E+14	38808.0

No	Reaction	A	E_a
51	$T3XC_6H_9-1E34CH=$ $P7XC_7H_{10}-1E-3-CH_2-4-C_2H_5$	4.87E+14	42285.6
52	$P6XC_6H_9-1E34CH=P1XCH_2-2-HD$	1.11E+12	15016.5
53	$P6XC_6H_9-1E45CH=S3XC_6H_9-1E45CH$	9.68E+11	17237.6
54	$P6XC_6H_9-1E45CH=P8XC_8H_{14}-1E-4-C_2H_3$	6.32E+13	30728.1
55	$P6XC_6H_9-1E45CH=S4XC_{10}H_{17}-19E$	5.08E+13	28188.4
56	$S3XC_6H_9-1E45CH=P9XC_9H_{14}-13E5M$	5.08E+13	28188.4
57	$S3XC_6H_9-1E45CH=S9XC_{10}H_{17}-13E$	1.44E+14	36596.3
58	$P6XC_6H_9-1E45CH=P1XCH_2-3-HD$	2.03E+14	39358.5
59	$S6XC_6H_9-1E56CH=S3XC_6H_9-1E56CH$	3.70E+11	20299.3
60	$S3XC_6H_9-1E56CH=C_4H_6+cC_6H_{11}$	7.08E+14	37532.2
61	$S6XC_6H_{10}-1E56CH=cC_6H_{10}+C_4H_7$	9.61E+13	31620.3
62	$S6XC_6H_{10}-1E56CH=P8XC_8H_{14}-1E-5-C_2H_3$	4.24E+13	31207.0
63	$S6XC_6H_{10}-1E56CH=P10XC_{10}H_{17}-15E$	5.56E+13	30624.7
64	$S6XC_6H_{10}-1E56CH=P1XCH_2-2-HD$	5.14E+10	7480.6
65	$S6XcC_{10}H_{17}-1E=S3XcC_{10}H_{17}-1E$	2.56E+12	30698.3
66	$S6XcC_{10}H_{17}-1E=S4XcC_{10}H_{17}-1E$	3.24E+12	37146.7
67	$S6XcC_{10}H_{17}-1E=P10XC_{10}H_{17}-16E$	2.47E+14	30267.0
68	$S6XcC_{10}H_{17}-1E=P10XC_{10}H_{17}-17E$	9.27E+13	29768.3
69	$S3XcC_{10}H_{17}-1E=P10XC_{10}H_{17}-13E$	3.13E+14	32498.7
70	$S4XcC_{10}H_{17}-1E=P10XC_{10}H_{17}-14E$	1.26E+14	26314.5
71	$S4XcC_{10}H_{17}-1E=S1XC_{10}H_{17}-19E$	1.90E+14	36963.9
Decomposition and isomerization of alkenyl radicals			
72	$S9XC_{10}H_{17}-13E=S5XC_{10}H_{17}-13E$	6.09E+10	9811.0
73	$S9XC_{10}H_{17}-13E=S6XC_{10}H_{17}-13E$	2.95E+11	23876.2
74	$S5XC_{10}H_{17}-13E=C_6H_8-135E+pC_4H_9$	1.21E+15	43634.9
75	$S6XC_{10}H_{17}-13E=nC_3H_7+C_7H_{10}-136E$	6.79E+13	30376.3
76	$S6XC_{10}H_{17}-13E=nC_4H_5+C_6H_{12}-1E$	1.20E+14	38307.3
77	$S9XC_{10}H_{17}-13E=P7XC_7H_{11}-13E+C_3H_6$	1.03E+14	30654.5
78	$S9XC_{10}H_{17}-13E=S1XC_3H_4CH_3cC_6H_{10}$	4.85E+09	2915.8

No	**Reaction**	**A**	E_a
79	$S4XC_{10}H_{17}-19E=S3XC_{10}H_{17}-19E$	7.45E+10	11804.0
80	$S4XC_{10}H_{17}-19E=C_2H_3+C_8H_{14}-17E$	4.96E+14	39116.0
81	$S4XC_{10}H_{17}-19E=P5XC_5H_9-1E+C_5H_8-14E$	1.11E+14	38863.7
82	$S3XC_{10}H_{17}-19E=C_4H_6+P6XC_6H_{11}-1E$	4.42E+14	38774.2
83	$S4XC_{10}H_{17}-19E=C_3H_5P1XCH_2cC_6H_{10}$	4.68E+09	6995.1
84	$S1XC_{10}H_{17}-19E=S4XC_{10}H_{17}-19E$	2.26E+12	16804.6
85	$S1XC_{10}H_{17}-19E=S5XC_{10}H_{17}-19E$	6.76E+11	9389.9
86	$S1XC_{10}H_{17}-19E=C_2H_2+P8XC_8H_{15}-1E$	3.72E+13	35986.2
87	$S5XC_{10}H_{17}-19E=aC_3H_5+C_7H_{12}-16E$	3.29E+13	12961.5
88	$S5XC_{10}H_{17}-19E=C_4H_7+C_6H_{10}-15E$	9.02E+13	46117.0
89	$S1XC_{10}H_{17}-16E=S4XC_{10}H_{17}-16E$	3.24E+12	17429.9
90	$S1XC_{10}H_{17}-16E=S5XC_{10}H_{17}-16E$	6.73E+11	6522.8
91	$S1XC_{10}H_{17}-16E=C_2H_2+P1XC_8H_{15}-4E$	1.62E+15	35308.6
92	$S4XC_{10}H_{17}-16E=C_2H_3+C_8H_{14}-14E$	9.75E+13	38138.3
93	$S4XC_{10}H_{17}-16E=C_5H_8-14E+S1XC_5H_9-1E$	1.27E+14	38647.1
94	$S5XC_{10}H_{17}-16E=aC_3H_5+C_7H_{12}-13E$	5.97E+13	28838.2
95	$S1XC_{10}H_{17}-16E=S1XC_4H_8cC_6H_9$		
96	$P10XC_{10}H_{17}-17E=S6XC_{10}H_{17}-17E$	1.00E+12	15967.7
97	$P10XC_{10}H_{17}-17E=C_2H_4+S1XC_8H_{13}-17E$	3.52E+14	38887.5
98	$S6XC_{10}H_{17}-17E=C_4H_7+C_6H_{10}-13E$	3.82E+14	38315.2
99	$P10XC_{10}H_{17}-16E=C_2H_4+P8XC_8H_{13}-16E$	5.35E+13	22193.1
100	$P10XC_{10}H_{17}-16E=C_5H_9-1ES2XcC_5H_8$	2.66E+11	15865.6
101	$P10XC_{10}H_{17}-15E=S7XC_{10}H_{17}-15E$	1.94E+12	20372.8
102	$P10XC_{10}H_{17}-15E=P8XC_8H_{13}-15E+C_2H_4$	5.31E+14	31759.4
103	$S7XC_{10}H_{17}-15E=C_8H_{12}-137E+C_2H_5$	3.21E+14	38446.4
104	$P10XC_{10}H_{17}-15E=C_4H_7S2XcC_6H_{10}$	8.12E+10	10012.9
105	$P10XC_{10}H_{17}-15E=P1XC_5H_8-1EcC_5H_9$	2.56E+11	7133.8
106	$P10XC_{10}H_{17}-14E=S6XC_{10}H_{17}-14E$	2.48E+16	19796.7
107	$P10XC_{10}H_{17}-14E=S7XC_{10}H_{17}-14E$	9.24E+16	31228.8
108	$P10XC_{10}H_{17}-14E=P8XC_8H_{13}-14E+C_2H_4$	2.03E+19	38498.0

No	**Reaction**	**A**	E_a
109	$S6XC_{10}H_{17} - 14E = C_7H_{10} - 136E + nC_3H_7$	3.57E+14	38484.1
110	$S7XC_{10}H_{17} - 14E = C_8H_{12} - 147E + C_2H_5$	5.92E+13	30187.6
111	$S7XC_{10}H_{17} - 14E = S1XC_5H_7 - 14E + C_5H_{10} - 1E$	1.01E+14	52807.9
112	$P10XC_{10}H_{17} - 14E = S1XC_4H_6 - 3EcC_6H_{11}$	3.44E+15	15217.4
113	$P10XC_{10}H_{17} - 13E = S6XC_{10}H_{17} - 13E$	8.20E+11	16815.3
114	$P10XC_{10}H_{17} - 13E = S7XC_{10}H_{17} - 13E$	2.38E+12	24017.3
115	$P10XC_{10}H_{17} - 13E = P8XC_8H_{13} - 13E + C_2H_4$	4.89E+14	32135.0
116	$S6XC_{10}H_{17} - 13E = C_7H_{10} - 136E + nC_3H_7$	1.03E+14	30869.2
117	$S6XC_{10}H_{17} - 13E = C_6H_{12} - 1E + nC_4H_5$	2.14E+14	38955.1
118	$S7XC_{10}H_{17} - 13E = C_8H_{12} - 137E + C_2H_5$	4.86E+13	30591.0
119	$S7XC_{10}H_{17} - 13E = P5XC_5H_7 - 13E + C_5H_{10} - 1E$	1.28E+13	19306.2
120	$P9XC_9H_{14} - 13E5M = S6XC_9H_{14} - 13E5M$	1.98E+12	24555.8
121	$P9XC_9H_{14} - 13E5M = T5XC_9H_{14} - 13E5M$	2.55E+11	9748.6
122	$P9XC_9H_{15} - 13E5M = P7XC_7H_{10} - 13E5M + C_2H_4$	3.32E+14	31165.3
123	$S6XC_9H_{14} - 13E5M = C_6H_{12} - 2E + nC_4H_5$	1.83E+14	38196.0
124	$S6XC_9H_{14} - 13E5M = C_7H_9 - 136E5M + C_2H_5$	6.65E+13	30489.6
125	$S6XC_9H_{14} - 13E5M = C_9H_{14} - 135E + CH_3$	2.80E+13	27558.5
126	$T5XC_9H_{14} - 13E5M = C_6H_7 - 135E2M + nC_3H_7$	4.24E+14	42398.9
127	$P9XC_9H_{14} - 13E5M = S1XC_3H_4CH_3cC_6H_{10}$	9.74E+10	5928.0
128	$P8XC_8H_{14} - 3E - 4 - C_2H_3 = S5XC_8H_{14} - 3E - 4 - C_2H_3$	1.41E+12	18215.9
129	$P8XC_8H_{14} - 3E - 4 - C_2H_3 =$ $P6XC_6H_{10} - 3E - 4 - C_2H_3 + C_2H_4$	2.97E+14	30129.9
130	$S5XC_8H_{14} - 3E - 4 - C_2H_3 = C_6H_9 - 13E - 3 - C_2H_3 + C_2H_5$	1.91E+14	38706.7
131	$P8XC_8H_{14} - 3E - 4 - C_2H_3 = S1XC_3H_6C_2H_3cC_5H_8$	2.97E+11	6946.5
132	$P8XC_8H_{14} - 1E - 5 - C_2H_3 = S4XC_8H_{14} - 1E - 5 - C_2H_3$	2.82E+11	16426.0
133	$P8XC_8H_{14} - 1E - 5 - C_2H_3 = T5XC_8H_{14} - 1E - 5 - C_2H_3$	1.06E+12	17296.2
134	$P8XC_8H_{14} - 1E - 5 - C_2H_3 = P6XC_6H_{10} - 5 - C_2H_3 + C_2H_4$	9.06E+13	29134.3
135	$S4XC_8H_{14} - 1E - 5 - C_2H_3 = C_6H_{11} - 1E - 3 - C_2H_3 + C_2H_3$	1.06E+14	37695.2
136	$S4XC_8H_{14} - 1E - 5 - C_2H_3 = C_7H_{10} - 136E + nC_3H_7$	1.65E+13	25690.5
137	$S4XC_8H_{14} - 1E - 5 - C_2H_3 = C_8H_{14} - 14E + C_2H_3$	1.23E+14	36908.3

No	Reaction	A	E_a
138	$T5XC_8H_{14}-1E-5-C_2H_3=$ $C_5H_9-1E-2-C_2H_3+aC_3H_5$	6.80E+13	27731.4
139	$T5XC_8H_{14}-1E-5-C_2H_3=$ $C_6H_9-15E-2-C_2H_3+C_2H_5$	9.78E+14	39920.9
140	$P8XC_8H_{14}-1E-5-C_2H_3=C_4H_7S2XcC_6H_{10}$	5.98E+10	16024.4
141	$P8XC_8H_{14}-1E-4-C_2H_3=S5XC_8H_{14}-1E-4-C_2H_3$	9.73E+11	22550.7
142	$P8XC_8H_{14}-1E-4-C_2H_3=T4XC_8H_{14}-1E-4-C_2H_3$	1.21E+11	10797.8
143	$P8XC_8H_{14}-1E-4-C_2H_3=$ $P6XC_6H_{10}-1E-4-C_2H_3+C_2H_4$	1.70E+14	30165.7
144	$S6XC_8H_{14}-1E-4-C_2H_3=$ $C_6H_9-15E-3-C_2H_3+C_2H_5$	5.28E+13	29770.2
145	$S6XC_8H_{14}-1E-4-C_2H_3=C_7H_{12}-13E+aC_3H_5$	4.88E+12	16753.1
146	$S6XC_8H_{14}-1E-4-C_2H_3=C_8H_{14}-14E+C_2H_3$	7.78E+13	37806.5
147	$T4XC_8H_{14}-1E-4-C_2H_3=$ $C_6H_8-15E-3-CH_2+nC_3H_7$	1.42E+14	37496.5
148	$T4XC_8H_{14}-1E-4-C_2H_3=$ $C_7H_{12}-1E-3-CH_2+C_2H_3$	2.63E+15	48527.4
149	$P7XC_7H_{10}-1E-3-CH_2-4-C_2H_5=$ $T4XC_7H_{10}-1E-3-CH_2-4-C_2H_5$	1.57E+12	22312.3
150	$P7XC_7H_{10}-1E-3-CH_2-4-C_2H_5=$ $P5XC_5H_6-1E-3-CH_2-4-C_2H_5+C_2H_4$	8.33E+13	28878.0
151	$T4XC_7H_{10}-1E-3-CH_2-4-C_2H_5=$ $C_5H_5-14E-3-CH_2-4-C_2H_5+C_2H_5$	1.19E+15	36308.1
152	$T4XC_7H_{10}-1E-3-CH_2-4-C_2H_5=$ $C_6H_{10}-1E-34-CH_2+CH_3$	7.70E+14	40034.1
153	$P7XC_7H_{10}-1E-3-CH_2-4-C_2H_5=$ $C_2H_5-1-C_2H_3-2-S2XcC_6H_9$	8.42E+10	6452.0
154	$P1XC_{10}H_{17}-46E=T4XC_{10}H_{17}-46E$	3.09E+12	21708.2
155	$P1XC_{10}H_{17}-46E=P1XC_8H_{13}-24E+C_2H_4$	4.41E+13	13179.3
156	$T4XC_{10}H_{17}-46E=S1XC_5H_9-1E+C_5H_8$	2.41E+16	41371.5

No	**Reaction**	**A**	E_a
157	$P1XC_{10}H_{17} - 46E = S1XC_4H_8cC_6H_9 - 2E$	1.96E+11	6779.9
158	$P1XC_9H_{15} - 3E - 5 - CH_2 = T4XC_9H_{15} - 3E - 5 - CH_2$	5.19E+12	25811.7
159	$P1XC_9H_{15} - 3E - 5 - CH2 = S1XC_7H_{11} - 1E - 3 - CH_2 + C_2H_4$	1.06E+15	38923.3
160	$T4XC_9H_{15} - 3E - 5 - CH_2 = C_2H_5 + C_7H_{10} - 3 - CH_2$	7.18E+14	39513.5
161	$P1XC_9H_{15} - 3E - 5 - CH2 = C_4H_9T1XcC_6H_8 - 2E$	2.84E+11	8909.2
162	$P1XC_8H_{13} - 45 - CH_2 = S1XC_6H_{11} - 23 - CH_2 + C_2H_4$	3.30E+13	21897.0
163	$P1XC_8H_{13} - 45 - CH_2 = C_5H_9 - 1EcC_5H_8$	3.47E+11	11091.4
164	$P1XC_8H_{13} - 45 - CH_2 = C_3H_7 - 1 - CH_2 - 2 - T1XcC_6H_8$	3.16E+11	10498.6
Dissociation of alkenecyclohexane			
165	$C_6H_{10} - 1E56CH + H = S3XC_6H_9 - 1E56CH + H_2$	2.42E+14	8169.8
166	$C_6H_{10} - 1E56CH = P1XCH_2cC_6H_{11} + aC_3H_5$	2.78E+15	67413.8
167	$C_6H_{10} - 1E45CH + H = S3XC_6H_9 - 1E45CH + H_2$	1.77E+14	7933.3
168	$C_6H_{10} - 1E45CH = S2XMCH + aC_3H_5$	1.86E+15	64097.1
169	$C_6H_{10} - 1E34CH + H = C_6H_9 - 1E34CH + H_2$	1.68E+14	9175.9
Stepwize dehydrogenation of cyclic intermediate methylhydrindane			
170	$spiro - 4 - 5 - decane + H = S1Xspiro - 4 - 5 - decane + H_2$	2.75E+14	11058.0
171	$P1XCH_2 - 1 - HD = S8XHD - 1M$	2.26E+13	23437.0
172	$S8XHD - 1M = HD - 7E1M + H$	1.93E+14	36936.1
173	$HD - 7E1M + H = S6XHD - 7E1M + H_2$	2.84E+14	8837.9
174	$S6XHD - 7E1M = HD - 57E1M + H$	4.15E+14	45783.1
175	$HD - 57E1M + H = S4XHD - 57E1M + H_2$	3.59E+14	7734.8
176	$S4XHD - 57E1M = HD - 357E1M + H$	7.78E+13	52450.2
177	$HD - 357E1M + H = S2XHD - 357E1M + H_2$	2.32E+14	9973.6
178	$S2XHD - 357E1M = indene + CH_3$	1.56E+15	45224.7
179	$P1XCH_2 - 2 - HD = S4XHD2M$	2.30E+12	35566.9
180	$S4XHD2M = HD - 4E2M + H$	7.30E+13	35765.6
181	$HD - 4E2M + H = T1XHD - 4E2M + H_2$	1.21E+14	5798.5
182	$T1XHD - 4E2M = HD - 14E + CH_3$	9.64E+14	41441.1
183	$HD - 14E + H = S6XHD - 14E + H_2$	3.33E+14	9622.6

No	**Reaction**	**A**	E_a
184	$S6XHD-14E = HD-146E + H$	7.38E+14	49201.1
185	$HD-146E + H = S8XHD-146E + H_2$	3.51E+14	9834.1
186	$S8XHD-146E = indene + H$	4.47E+14	46321.6
187	$P1XCH_2-3-HD = T1XHD3M$	3.79E+12	23085.3
188	$T1XHD3M = HD-1bE3M + H$	1.27E+14	35332.4
189	$HD-1bE3M + H = S2XHD-1bE3M + H_2$	1.21E+14	7462.1
190	$S2XHD-1bE3M = HD-1b2E + CH_3$	7.85E+14	40620.4
191	$HD-1b2E + H = S6XHD-1b2E + H_2$	3.28E+14	6565.7
192	$S6XHD-1b2E = HD-1b26E + H$	1.08E+14	55401.1
193	$HD-1b26E + H = S7XHD-1b26E + H_2$	4.31E+14	5745.6
194	$S7XHD-1b26E = indene + H$	1.35E+14	33430.7
cyclohexane			
195	$C_2H_5-1-C_2H_3-2-S2XcC_6H_9 = C_2H_3cC_6H_9 + C_2H_5$	1.38E+15	37399.1
196	$C_3H_7-1-CH_2-2-T1XcC_6H_8 = CH_2-12-cC_6H_8$	9.31E+14	40678.0
197	$CH_2-12-cC_6H_8 = CH_2-2-CH_3cC_6H_7$	4.51E+13	94441.7
198	$CH_2-2-CH_3cC_6H_7 = DCH-15E$	4.92E+13	93887.3
199	$DCH-15E + H = S3XDCH-15E + H_2$	7.58E+14	6472.5
200	$S3XDCH-15E = o-xylene + H$	1.26E+14	30358.5
201	$C4H7S2XcC6H10 = cC6H10 + C4H7$	2.88E+14	31825.0
202	$C_4H_9T1XcC_6H_8-2E = CH_2cC_6H_8-2E + nC_3H_7$	8.92E+14	39052.5
203	$CH_2cC_6H_8-2E = MCH-15E$	2.72E+13	94698.0
204	$MCH-15E + H = S3XMCH-15E + H_2$	3.76E+14	6363.4
205	$S3XMCH-15E = A1CH_3 + H$	5.01E+13	31612.4
206	$S1XC_3H_4CH_3-2cC_6H_{10} = C_3H_5-CH_3-2-S6XcC_6H_{10}$	1.11E+13	58294.5
207	$C_3H_5-CH_3-2-S6XcC_6H_{10} = MCH-2E + aC_3H_5$	2.12E+13	22687.9
208	$MCH-2E + H = T1XMCH-2E + H_2$	1.72E+14	5798.6
209	$T1XMCH-2E = MCH-15E + H$	3.18E+14	51241.9
210	$S1XC_3H_4CH_3cC_6H_{10} = C_3H_5P1XCH_2cC_6H_{10}$	9.60E+13	49976.1
211	$C_3H_5P1XCH_2cC_6H_{10} = C_3H_5CH_3S3XcC_6H_9$	1.77E+13	39930.8
212	$C_3H_5CH_3S3XcC_6H_9 = C_3H_5CH_3cC_6H_8-2E + H$	1.89E+14	39008.7

No	**Reaction**	**A**	E_a
213	$C_3H_5CH_3cC_6H_8-2E+H=C_3H_5CH_3S4XcC_6H_8-2E+H_2$	3.11E+14	9022.7
214	$C_3H_5CH_3S4XcC_6H_8-2E=C_3H_5CH_3cC_6H_8-24E+H$	7.39E+14	51490.3
215	$C_3H_5CH_3cC_6H_8-24E+H=C_3H_5CH_3S6XcC_6H_8-24E+H_2$	2.46E+14	6644.2
216	$C_3H_5CH_3S6XcC_6H_8-24E=A1CH_3+aC_3H_5$	2.29E+13	13541.4
217	$S1XC_4H_6-3EcC_6H_{11}=C_2H_3cC_6H_{11}+C_2H_3$	3.85E+14	37301.7
218	$C_2H_3cC_6H_{11}+H=C_2H_3T1XcC_6H_{10}+H_2$	8.80E+13	7117.6
219	$C_2H_3T1XcC_6H_{10}=C_2H_3cC_6H_9+H$	1.63E+15	49666.1
220	$S1XC_4H_8cC_6H_9=C_2H_3cC_6H_9+C_2H_5$	8.51E+14	39807.6
221	$C_2H_3cC_6H_9+H=C_2H_3S3XcC_6H_8+H_2$	3.69E+14	6372.4
222	$C_2H_3S3XcC_6H_8=C_2H_3cC_6H_7-13E+H$	1.77E+15	57068.4
223	$C_2H_3cC_6H_7-13E+H=C_2H_3S5XcC_6H_6-13E+H_2$	3.20E+14	7980.2
224	$C_2H_3S5XcC_6H_6-13E=A1C_2H_3+H$	1.14E+14	33394.9
225	$S1XC_4H_8cC_6H_9-2E=C_2H_3cC_6H_9-2E+C_2H_5$	1.37E+14	29851.7
226	$C_2H_3cC_6H_9-2E+H=C_2H_3T1XcC_6H_8-2E+H_2$	1.60E+14	6701.0
227	$C_2H_3T1XcC_6H_8-2E=C_2H_3cC_6H_7-15E+H$	2.73E+14	60021.4
228	$C_2H_3cC_6H_7-15E+H=C_2H_3S3XcC_6H_6+H_2$	4.13E+14	5963.8
229	$C2H_3S3XcC_6H_6-15E=A1C_2H_3+H$	3.69E+14	35674.2
cyclopentane			
230	$C_5H_9-1EcC_5H_8=C_5H_9-1EcC_5H_7+H$	1.04E+14	44743.8
231	$C_5H_9-1EcC_5H_7+H=C_5H_9-1EcC_5H_6+H_2$	2.23E+14	6026.0
232	$C_5H_9-1EcC_5H_6=C_5H_9-1EcC_5H_5+H$	6.59E+13	51625.5
233	$C_5H_9-1EcC_5H_5=T1XC_5H_5+S2XC_5H_9-1E$	9.68E+16	110122.7
234	$C_5H_9-1ES2XcC_5H_8=cC_5H_8+S1XC_5H_9-1E$	4.50E+14	37876.0
235	$C_5H_9-4ES2XcC_5H_8=cC_5H_8+P5XC_5H_9-1E$	2.19E+14	29494.0
236	$P1XC_5H_8-1EcC_5H_9=C_2H_3cC_5H_9+aC_3H_5$	2.29E+13	20505.9
237	$C_2H_3cC_5H_9+H=C_2H_3T1XcC_5H_8+H_2$	8.10E+13	8904.0
238	$C_2H_3T1XcC_5H_8=C_2H_3cC_5H_7+H$	1.65E+14	47269.5
239	$C_2H_3cC_5H_7+H=C_2H_3S3XcC_5H_6+H_2$	2.80E+14	7309.5
240	$C_2H_3S3XcC_5H_6=C_2H_3cC_5H_5+H$	1.40E+14	53000.6
241	$C_2H_3cC_5H_5=T1XC_5H_5+C_2H_3$	1.15E+17	113540.7

No	**Reaction**	**A**	E_a
242	$P1XCH_2 - C_4H_9 - cC_5H_6 - 2E = CH_2cC_5H_6 + pC_4H_9$	1.69E+14	27236.6
243	$CH_2cC_5H_6 = cC_5H_5 - 13E2M$	1.54E+13	83933.4
244	$S1XC_3H_6C_2H_3cC_5H_8 = C_2H_3C_2H_3cC_5H_8 + CH_3$	8.43E+13	31342.1
245	$C_2H_3C_2H_3cC_5H_8 + H = C_2H_3C_2H_3S2XcC_5H_8 + H_2$	2.80E+14	13284.4
246	$C_2H_3C_2H_3S2XcC_5H_8 = C_2H_3cC_5H_7 + C_2H_3$	3.45E+14	33255.8
olefinic decalin			
247	$decalin - 1bE + H = S2Xdecalin - 1bE + H_2$	1.12E+15	6679.8
248	S2Xdecalin-1bE = decalin-1b2E+H	8.59E+14	50459.0
249	$decalin - 1b2E + H = S4Xdecalin - 1b2E + H_2$	3.79E+14	6370.2
250	S4Xdecalin-1b2E = tetralin+H	1.56E+14	31290.5
251	$tetralin + H = S7Xdecalin - 1b24E + H2$	6.25E+14	10109.7
252	S7Xdecalin-1b24E = decalin-1b247E+H	5.95E+14	46242.1
253	$decalin - 1b247E + H = S9Xdecalin - 1b247E + H_2$	3.54E+14	10943.7
254	S9Xdecalin-1b247E = naphthalene+H	1.40E+14	34815.7
255	$decalin - 1bE = C_2H_4 + CH_2 - 12 - cC_6H_8$	1.43E+15	67296.5
256	$decalin - 1E + H = T6Xdecalin - 1E + H_2$	1.66E+14	5494.0
257	T6Xdecalin-1E = decalin-15E+H	1.76E+14	51432.7
258	$decalin - 15E + H = S3Xdecalin - 15E + H_2$	8.24E+14	10771.6
259	S3Xdecalin-15E = tetralin+H	1.31E+14	30447.9
260	$decalin - 1E = C_2H_4 + C_2H_3cC_6H_9$	4.60E+15	68697.5
261	$decalin - 2E + H = T1Xdecalin - 2E + H_2$	1.24E+14	5889.9
262	T1Xdecalin-2E = decalin-1b2E+H	1.67E+14	48555.2
263	$decalin - 3E + H = S2Xdecalin - 3E + H_2$	4.56E+14	7499.7
264	S2Xdecalin-3E = decalin-13E+H	9.29E+13	48692.4
265	$decalin - 13E + H = T6Xdecalin - 13E + H_2$	8.51E+14	4097.4
266	T6Xdecalin-13E = tetralin+H	1.56E+14	31290.5
267	$decalin - 3E = C_4H_6 + cC_6H_{10}$	1.64E+15	69561.9

Note $k(T) = A\exp(-E_a/RT)$, unit is cm^3, mol, s, cal.

5.4 Comparison of isomerization and unimolecular decomposition channel of decalin with cyclohexane, methylcyclohexane, iso-propyl cyclohexane, 135-trimethylcyclohexane

In the table 5.6 we compare energy barriers of isomerization and unimolecular decomposition channel of all above-mentioned cyclohexane derivatives. From the table we can see that decalin has few kcal/mol higher C-H dissociation energy compared to cyclohexane.

Table 5.6: Comparison of energy barrier of isomerization and unimolecular decomposition channel of cyclohexane (CH), methylcyclohexane (MCH), isppropylcyclohexane (IPCH), cis-trimethylcyclohexane (T135CH), trans trimethylcyclohexane (T135CH-t) and decalin. Energy unit: kcal/mol.

	CH[13]	MCH[16]	IPCH	T135CH	135TCH-t	decalin
C-H dissociation	97.8					97.0/ 102.4 /99.9
CH_3 elimination		84.0	83.2/ 81.6(C_3H_7 elimination)	85.6	82.5(axial) /85.3(equ.)	
TS of C1-C2 ring opening	88.7	85.0	85.9	86.3	87.9	85.4
TS of C2-C3 ring opening		89.0	88.0			84.0
TS of C3-C4 ring opening		89.0	87.6			86.9

IPCH has low energetic unicomelucar decomposition channel among the cyclohexane derivatives. From this table we can conclude that single-side chain alkylcyclohexane has lowest energy barrier for unimolecular decomposition channel as it has low barrier alkyl group elimination channel. For ring-opening isomerization channel decalin has lowest energy barrier although energy difference is within 2 kcal/mol.

Figure 5.48 shows the rate of unimolecular decomposition channel of different

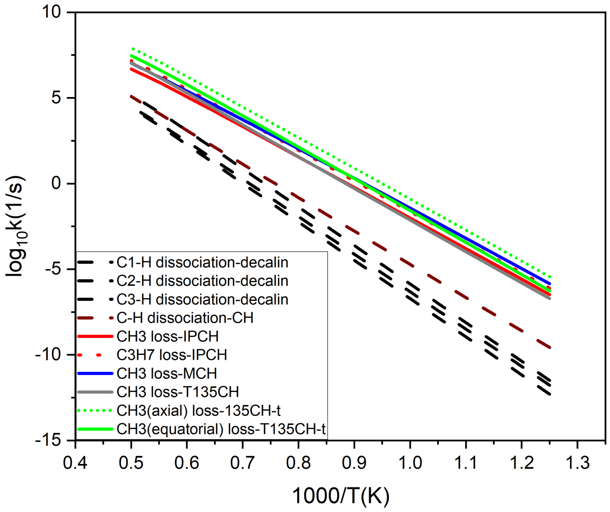

Figure 5.48: Comparison of rate constant of unimolecular decomposition channel of different cyclohexane derivatives. Cyclohexane and methylcyclohexane data talen from reference

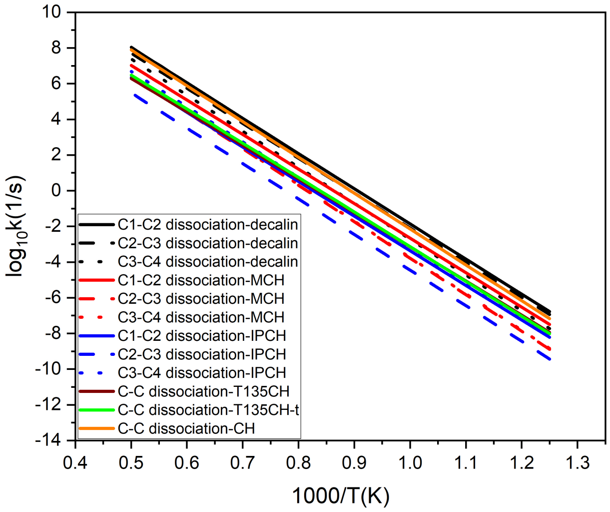

Figure 5.49: Comparison of rate constant of ring opening isomerization channel of different cyclohexane derivatives. Cyclohexane and methylcyclohexane data talen from reference

cyclohexane derivatives. We can see that the rate constant of CH_3 elimination channel is much faster than H atom elimination reaction. Axial CH_3 loss channel of T135CH-t is the fastest process among them. Figure 5.49 shows rate of ring opening isomerization channel of different cyclohexane derivatives. Ring opening of decalin has fastest process among them followed by cyclohexane. With the alkyl group substitution at cyclohexane ring, the rate of ring opening channel keep decreasing.

5.5 Conclusion

In this work, we have calculated the rate constants of decalin decomposition at the temperature range from 800 to 8000 K using the VTST and TST methods combined with quantum chemical calculations, and the detailed reaction mechanism has been analyzed. We found that for decalin the initial decomposition channel is the the ring-opening channel. We proposed the reaction mechanism of all the arometic products which is observed during experiments. All other important elementary reactions also have been investigated. Finally, reaction rate constants for all 267 elementary reactions in the Arrhenius expression have been derived in the temperature range of 800-2000K, which can be used in kinetic modeling studies of pyrolysis and combustion of decalin.

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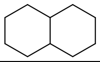
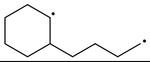
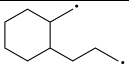
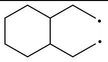
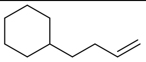
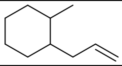
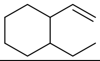
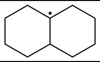
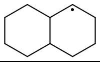
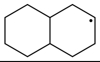
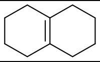
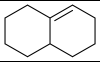
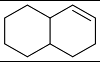
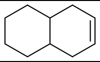
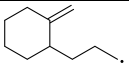
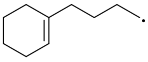
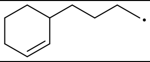
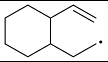
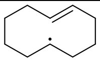
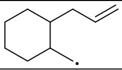
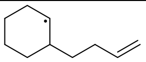
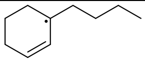
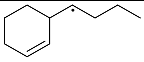
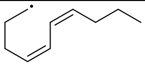
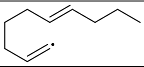
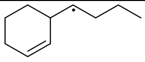
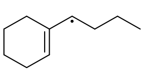
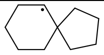
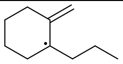
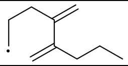
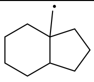
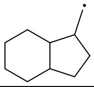
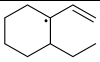
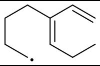
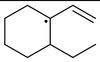
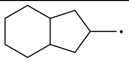
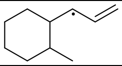
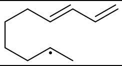
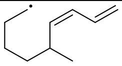
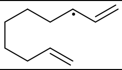
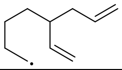
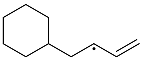
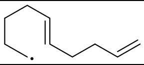
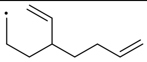
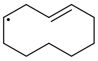
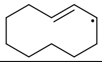
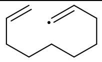
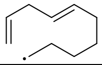
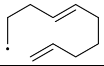
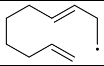
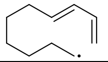
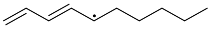
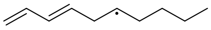
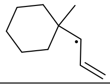
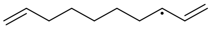
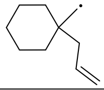
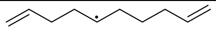
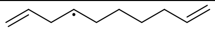
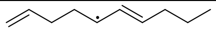
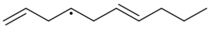
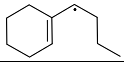
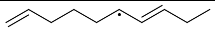
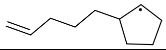
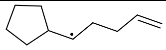
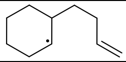
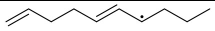
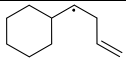
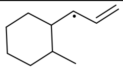
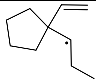
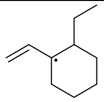
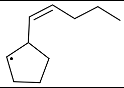
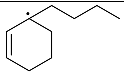
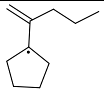
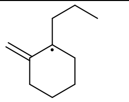
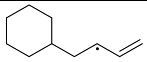
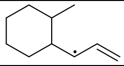
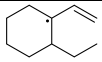
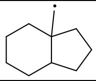
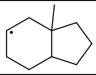
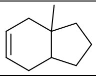
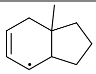
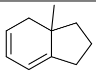
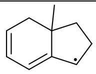
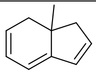
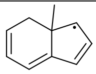
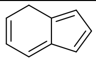
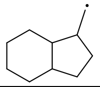
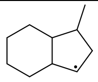
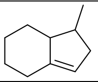
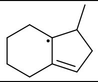
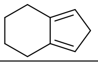
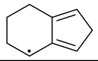
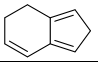
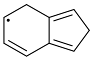
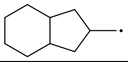
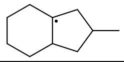
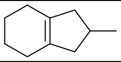
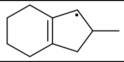
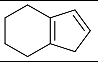
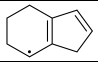
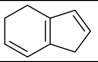
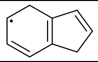
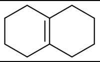
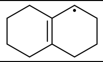
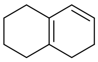
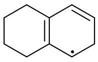
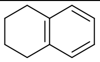
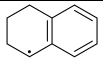
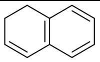
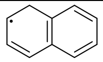
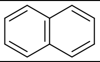
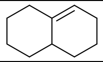
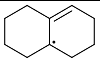
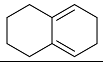
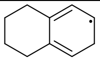
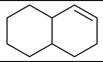
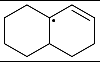
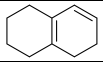
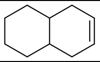
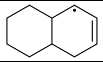
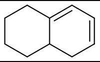
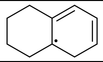
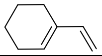
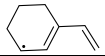
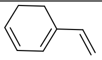
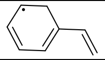
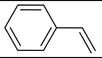
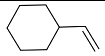
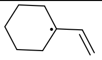
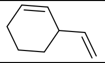
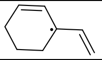
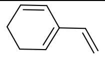
5.6 Additional Information

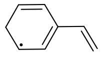
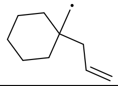
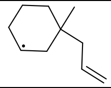
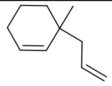
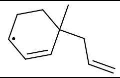
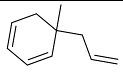
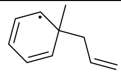
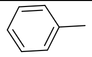
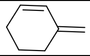
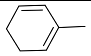
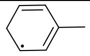
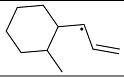
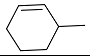
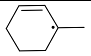
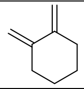
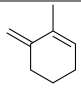
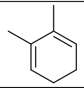
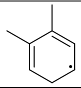
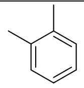
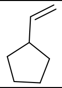
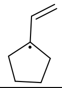
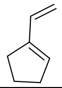
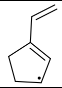
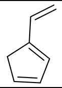
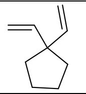
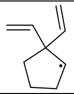
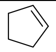
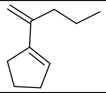
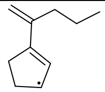
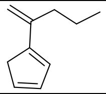
5.6.1 Nomenclature and structure of the species in the mechanism

Structure and nomenclature of the species used in the mechanism are given here.

formula	nomenclature	structure	formula	nomenclature	structure
$C_{10}H_{18}$	decalin		$C_{10}H_{18}$	Biradical1	
$C_{10}H_{18}$	Biradical2		$C_{10}H_{18}$	Biradical3	
$C_{10}H_{18}$	C6H10-1E56CH		$C_{10}H_{18}$	C6H10-1E45CH	
$C_{10}H_{18}$	C6H10-1E34CH		$C_{10}H_{17}$	T1Xdecalin	
$C_{10}H_{17}$	S2Xdecalin		$C_{10}H_{17}$	S3Xdecalin	
$C_{10}H_{16}$	decalin-1bE		$C_{10}H_{16}$	decalin-1E	
$C_{10}H_{16}$	decalin-2E		$C_{10}H_{16}$	decalin-3E	
$C_{10}H_{17}$	P6XC6H9-1E23CH		$C_{10}H_{17}$	P6XC6H9-1E12CH	
$C_{10}H_{17}$	P4XC4H8cC6H9		$C_{10}H_{17}$	P6XC6H9-1E34CH	
$C_{10}H_{17}$	S6XcC10H17-1E		$C_{10}H_{17}$	P6XC6H9-1E45CH	
$C_{10}H_{17}$	S6XC6H9-1E56CH		$C_{10}H_{17}$	TXC4H8cC6H9	
$C_{10}H_{17}$	S1XC4H8cC6H9		$C_{10}H_{17}$	P1XC10H17-46E	
$C_{10}H_{17}$	S1XC10H17-16E		$C_{10}H_{17}$	P1XC9H15-3E-5-CH2	
$C_{10}H_{17}$	S1XC6H9-1E12CH		$C_{10}H_{17}$	S1Xspiro-4-5-DN	
$C_{10}H_{17}$	T3XC6H9-1E23CH		$C_{10}H_{17}$	P1XC8H13-45-CH2	
$C_{10}H_{17}$	P1XCH2-1-HD		$C_{10}H_{17}$	P1XCH2-2-HD	
$C_{10}H_{17}$	T3XC6H9-1E34CH		$C_{10}H_{17}$	P8XC8H14-3E-4-C2H3	
$C_{10}H_{17}$	P7XC7H10-1E-3-CH2-4-C2H5		$C_{10}H_{17}$	P1XCH2-3-HD	
$C_{10}H_{17}$	S3XC6H9-1E45CH		$C_{10}H_{17}$	S9XC10H17-13E	
$C_{10}H_{17}$	P9XC9H14-13E5M		$C_{10}H_{17}$	S4XC10H17-19E	
$C_{10}H_{17}$	P8XC8H14-1E-4-C2H3		$C_{10}H_{17}$	S3XC6H9-1E56CH	
$C_{10}H_{17}$	P10XC10H17-15E		$C_{10}H_{17}$	P8XC8H14-1E-5-C2H3	

$C_{10}H_{17}$	S4XcC10H17-1E		$C_{10}H_{17}$	S3XcC10H17-1E	
$C_{10}H_{17}$	S1XC10H17-19E		$C_{10}H_{17}$	P10XC10H17-14E	
$C_{10}H_{17}$	P10XC10H17-16E		$C_{10}H_{17}$	P10XC10H17-17E	
$C_{10}H_{17}$	P10XC10H17-13E		$C_{10}H_{17}$	S5XC10H17-13E	
$C_{10}H_{17}$	S6XC10H17-13E		$C_{10}H_{17}$	S1XC3H4CH3cC6H10	
$C_{10}H_{17}$	S3XC10H17-19E		$C_{10}H_{17}$	C3H5P1XCH2cC6H10	
$C_{10}H_{17}$	S5XC10H17-19E		$C_{10}H_{17}$	S4XC10H17-19E	
$C_{10}H_{17}$	S5XC10H17-16E		$C_{10}H_{17}$	S4XC10H17-16E	
$C_{10}H_{17}$	S1XC4H8cC6H9		$C_{10}H_{17}$	S6XC10H17-17E	
$C_{10}H_{17}$	C5H9-1ES2XcC5H8		$C_{10}H_{17}$	P1XC5H8-1EcC5H9	
$C_{10}H_{17}$	C4H7S2XcC6H10		$C_{10}H_{17}$	S7XC10H17-15E	
$C_{10}H_{17}$	S1XC4H6-3EcC6H11		$C_{10}H_{17}$	S1XC3H4CH3cC6H10	
$C_{10}H_{17}$	S1XC3H6C2H3cC5H8		$C_{10}H_{17}$	C2H5-1-C2H3-2-S2XcC6H9	
$C_{10}H_{17}$	S1XC4H8cC6H9-2E		$C_{10}H_{17}$	C4H9T1XC6H8-2E	
$C_{10}H_{17}$	C5H9-1EcC5H8		$C_{10}H_{17}$	C3H7-1-CH2-2-T1XcC6H8	
$C_{10}H_{17}$	S3XC6H9-1E56CH		$C_{10}H_{17}$	S3XC6H9-1E45CH	
$C_{10}H_{17}$	S3XC6H9-1E34CH		$C_{10}H_{17}$	P1XCH2-1-HD	
$C_{10}H_{17}$	S8XHD-1M		$C_{10}H_{16}$	HD-7E1M	
$C_{10}H_{15}$	S6XHD-7E1M		$C_{10}H_{14}$	HD-57E1M	
$C_{10}H_{13}$	S4XHD-57E1M		$C_{10}H_{12}$	HD-357E1M	
$C_{10}H_{11}$	S2XHD-357E1M		C_9H_8	indene	

$C_{10}H_{17}$	P1XCH2-2-HD		$C_{10}H_{17}$	S4XHD2M	
$C_{10}H_{16}$	HD-4E2M		$C_{10}H_{15}$	T1XHD-4E2M	
$C_{9}H_{12}$	HD-14E		$C_{9}H_{11}$	S6XHD-14E	
$C_{9}H_{10}$	HD-146E		$C_{9}H_{9}$	S8XHD-146E	
$C_{10}H_{17}$	P1XCH2-3-HD		$C_{10}H_{17}$	T1XHD3M	
$C_{10}H_{16}$	HD-1bE3M		$C_{10}H_{15}$	S2XHD-1bE3M	
$C_{9}H_{12}$	HD-1b2E		$C_{9}H_{11}$	S6XHD-1b2E	
$C_{9}H_{10}$	HD-1b26E		$C_{9}H_{9}$	S7XHD-1b26E	
$C_{10}H_{16}$	decalin-1bE		$C_{10}H_{15}$	S2Xdecalin-1bE	
$C_{10}H_{14}$	decalin-1b2E		$C_{10}H_{13}$	S4Xdecalin-1b2E	
$C_{10}H_{12}$	tetralin		$C_{10}H_{11}$	S7Xdecalin-1b24E	
$C_{10}H_{10}$	decalin-1b247E		$C_{10}H_{9}$	S9Xdecalin-1b247E	
$C_{10}H_{8}$	naphthalene		$C_{10}H_{16}$	decalin-1E	
$C_{10}H_{15}$	T6Xdecalin-1E		$C_{10}H_{14}$	decalin-15E	
$C_{10}H_{13}$	S3Xdecalin-15E		$C_{10}H_{16}$	decalin-2E	
$C_{10}H_{15}$	T1Xdecalin-2E		$C_{10}H_{14}$	decalin-1b2E	
$C_{10}H_{16}$	decalin-3E		$C_{10}H_{15}$	S2Xdecalin-3E	
$C_{10}H_{14}$	decalin-13E		$C_{10}H_{13}$	T6Xdecalin-13E	
$C_{8}H_{12}$	C2H3cC6H9		$C_{8}H_{11}$	C2H3S3XcC6H8	
$C_{8}H_{10}$	C2H3cC6H7-13E		$C_{8}H_{9}$	C2H3S5XcC6H6-13E	
$C_{8}H_{8}$	A1C2H3		$C_{8}H_{14}$	C2H3cC6H11	
$C_{8}H_{13}$	C2H3T1XcC6H10		$C_{8}H_{12}$	C2H3cC6H9-2E	
$C_{8}H_{11}$	C2H3T1XcC6H8-2E		$C_{8}H_{10}$	C2H3cC6H7-15E	

C_8H_9	C2H3S3XcC6H6-15E		$C_{10}H_{17}$	C3H5P1XCH2cC6H10	
$C_{10}H_{17}$	C3H5CH3S3XcC6H9		$C_{10}H_{16}$	C3H5CH3cC6H8-2E	
$C_{10}H_{15}$	C3H5CH3S4XcC6H7-2E		$C_{10}H_{14}$	C3H5CH3cC6H6-24E	
$C_{10}H_{13}$	C3H5CH3cC6H5-24E		C_7H_8	A1CH3	
C_7H_{10}	CH2cC6H8-2E		C_7H_{10}	MCH-15E	
C_7H_9	S3XMCH-15E		$C_{10}H_{17}$	C3H4-CH3-2-S6XcC6H10	
C_7H_{12}	MCH-2E		C_7H_{11}	T1XMCH-2E	
C_8H_{12}	CH2-12-cC6H8		C_8H_{12}	CH2-2-CH3cC6H8	
C_8H_{12}	DCH-15E		C_8H_{11}	S3XDCH-15E	
C_8H_{10}	o-xylene		C_7H_{12}	C2H3cC5H9	
C_7H_{11}	C2H3T1XcC5H8		C_7H_{10}	C2H3cC5H7	
C_7H_9	C2H3S3XcC5H6		C_7H_8	C2H3cC5H5	
C_9H_{14}	C2H3C2H3cC5H8		C_9H_{13}	C2H3C2H3S2XcC5H7	
C_5H_8	cC5H8		$C_{10}H_{16}$	C5H9-1EcC5H7	
$C_{10}H_{15}$	C5H9-1EcC5H6		$C_{10}H_{14}$	C5H9-1EcC5H5	

Chapter 6

Computational investigation on $C_2 + C_2$ addition reaction: importance of spin state in combustion

6.1 Introduction

The interest of studying pure carbon molecules was increasing from last few decades. These molecules have been detected in astronomical sources e.g. in the atmospheres of carbon stars, Sun , Comets and diffuse interstellar cloud[1,2]. It became an exciting field, due to the development of methods for the production of cold cluster beams(which are studied by mass spectrometric detection and mass-selected spectroscopy); improvement in the accuracy of theoretical calculations and the application of those techniques in structures and electronic states, ionization potentials, oscillator strengths, vibrational frequencies, etc.; unexpected, complexities in the properties and spectroscopy of these C_n species (e.g. quasi-linearity in C_3,linear and rhombic isoenergetic isomers of C_4); awareness of the possible astrophysical significance of these species as contributors to the formation of the long-chain cyanopolyynes, carbon dust, polycyclic aromatic hydrocarbons, and diffiuse interstellar bands; and involvement of large C_n clusters in the nucleation of carbon particles and formation of soot in hydrocarbon combustion[1]. So, the study of poly-carbons and their ions is important. Now here we are mainly focusing on the elementary reactions involving C_2 radicals and other small carbon species like C, C_3 and C_4. The largest fraction of the carbon present in the universe is in the form of neutral or ionic C and the second largest molecular form is CO, while among small carbon cluster C_2, C_3 and C_5 are present in astrophysical sources. C_2 is confirmed by detection of absorption line of the (1-0) Phillips band in the near-infrared region[3], C_3 (antisymmetric stretch is IR active) is detected by vibration-rotation lines in the infrared region[4] and C_5 (antisymmetric stretch is IR active) molecule has been identified similarly in the infrared spectrum[5] and these are important reactants in the chemistry of the interstellar medium. Studies of Gingerich et al.[6–8] shows that C, C_2, and C_3 are the primary components of equilibrium carbon vapour over graphite at $2000 - 5000K$ temperatures range. C_3 was a major component, accounting for about 80% of the vapour pressure at $2700K$, while C and C_2 were present at about 14% and 6%, respectively. The larger clusters (C_4-C_7) existed only in trace quantities at these temperatures, accounting for less than 0.1% of the pure carbon species. These species are reaction intermediates in a wide variety of chemical systems involving hydrocarbons, including photolysis, electric discharges, and combustion systems[2] (e.g., soot formation in hot flames, diamond synthesis from gas phase pyrolysis, the formation and decay of fullerene[9–11]). C_2 and C_3 are well-characterized of all the carbon clusters as spectroscopy of these species has been studied for several years. Again C_3 is described as "one of the most well-characterized nonrigid triatomic in existence" by Rohlfing et al. (1995)[12].

6.1.1 Geometry and Spectroscopy of C_2, C_3 and C_4

From the beginning of molecular orbital calculations, we know that the carbon clusters smaller than C_{10} possess low-energy linear structures. Cumulenic bonding with nearly equivalent bond lengths and acetylenic bonding, with alternating bond lengths. Cumulenic bonding was predicted to be the preferred one than acetylenic bonding.

C_2:

The C_2 exists in a singlet ($X^1\sum_g^+$) ground electronic state, and it has low lying triplet ($a^3\prod_u$) state (716 cm^{-1}) above the ground state[2]). The electornic state configuration are the following:

$$X^1\sum_g^+ : (1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4$$

$$a^3\prod_u : (1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^3(1\sigma_g)^1$$

Apart from those two states, another two low lying states are present: $b^3\sum_g^-$ and $A^1\prod_u$ which are 6434 cm^{-1} and 8391 cm^{-1} above the ground state, respectively[2]. In addition to these low-lying states, around 14 other electronic states have been observed for C_2. For C_2 many well-known band systems have been characterised. The most prominent of these is the Swan system ($d^3\prod_g - a^3\prod_u$) at 19400 cm^{-1}. Others include the Phillips bands ($A^1\prod_u - X^1\sum_g^+$) and the Mulliken bands ($D^1\sum_u^+ - X^1\sum_g^+$) at 43227 cm^{-1}.

C_3:

For C_3 both linear and cyclic structures are possible , although the linear structure is most stable one. Even though C_3 has a remarkably low bending frequency, there appears to be no experimental evidence for cyclic isomers[2]. Schleyer et al. theoretically proposed that a cyclic structure is possible.[13].

For the linear C_3 ground state is singlet ($X^1\sum_g^+$) and next exited state is a triplet ($^3\prod_u$). The electornic state configuration are the following:

$$X^1\sum_g^+ : KKK(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(1\pi_u)^4(2\sigma_u)^2$$

$$^3\prod_u : KKK(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(1\pi_u)^4(2\sigma_u)(1\pi_g)$$

For the cyclic C_3 ground state is triplet ($^3A_2^{'}$) and next exited state is a singlet ($^1A_1$). The electornic state configuration are the following:

$$^3A_2^{'} : KKK(a_1^{'})^2(e^{'})^4(a_1^{'})^2(a^{''})^2(e^{'})^2$$

$$^1A_1 : KKK(a_1)^2(a_1)^2(b_2)^2(b_1)^2(a_1)^2(a_1)^2$$

The energy difference of ground state cyclic C_3 from its ground state linear structure is 24.4 kcal/mol[13].

C_4:

C_4 has both linear and cyclic structure. Most theoretical calculation shows that there are two lowest energy structures, the cumulenic linear chain, and a bicyclic rhombic (2) structure[2]. However, there has been considerable disagreement over which of these structures is the true global minimum. By using CASSCF and MRCI levels of theory it was found that the cumulenic linear structure is slightly lower in energy than the rhombic[14,15]. On the other hand for CCSD(T) level of theory also relative energies to be extremely sensitive to the size of the basis and the type of basis used, the effect of increasing the polarisation of the basis functions, as well as the inclusion of triple excitations, tended to favour the rhombic. The highest-level calculations (CCSD(T)/PVQZ) predict that rhombic isomer is the lowest energy structure, but only by about 1 kcal/mol[2]. However, the absolute relative energy position of linear-C4/rombic-C4 is not yet established.

The linear C_4 exists in a triplet $(X^3\sum g^-)$ ground state and the next exited state is a singlet $(a^1\Delta g)$.The rhombic C_4 exists in a singlet(X^1Ag) ground state and the next exited state is a triplet (a^3B_1u). There is another possible cyclic structure of C_4, C_3-monocyclic species. By earlier theoretical studies it is found that this structure has a singlet ground state, and it is 30 $kcalmol^{-1}$(MP4/6-31G*//HF/6-31G* level of theory) above the two almost isoenergetic isomers[16].

6.1.2 Elementary reaction involving C_2

As the elementary reaction involving C_2 and other small carbon species like C, C_3 and C_4 plays important role in high temperature chemistry of hydrocarbon, there are few studies to understand those reactions involving small carbon species. In 1962, Tsang et al. measured the production of C_2 (lowest vibration level of $^3\prod u$ state had been measured by absorbance spectroscopy, i.e. they measure swan band at 5165 $\AA$ during the pyrolysis (temperature range was 2600-3600K) of ethylene[17]. By calculation they found that C, C_3, C_4 form from ethylene by various pathways and C_3 had relatively large concentration compared to C_2 although they did not observe its (i.e.C_3) well-known spectrum at 4050 Å. In 1975, Beck et al. had studied kinetics of formation and decay of C_2 from high-temperature pyrolysis of acetylene (temperatures range 4860-6920K)[18]. They measured emission spectrum of swan system of C_2 at 514 nm. They had considered 12 reactions to analyse the kinetics of formation and decay of C_2 and none of those reactions involved other pure carbon molecules (e.g.C_3, C_4 etc.). Later in 1992, Kiefer et al. did kinetic/ thermochemical model for the high-temperature radical chain decomposition of acetylene (mechanism was tested by time-of-flight mass spectra in C_2H_2/H_2 mixtures over 1600-2100 K and laser schlieren experiments in C_2H_2, covering 2700-3500 K[19]. In their kinetic model, they considered C_2, C_4, and C_6 pure carbon molecules comprising of 86 reactions of which only two reactions are associated with only pure carbon molecules (i.e $2C_2 + M \rightarrow C_4$ (M= third body) and $C_2 + C_4 \rightarrow C_6$). They mentioned that odd carbon species, especially C_3 must appear in high-temperature pyrolysis of C_2H_2 but they did not know the rate and mechanism of that appearance. They found disagreement between their experiment and kinetic model, and they indicated that this was because of the greater contribution from pure carbon molecules (C_3, C_4 etc) and the reactions of these species and their rates are effectively unknown. In 1995, Roth et al. measured C_2 formation (used ring dye laser for C_2 concentration measurement, and they also measured swan system) during high-temperature pyrolysis of fullerene C_{60}[20]. They observed that higher temperature leads to a higher yield of C_2 and reached a maximum concentration.

At a temperature greater than 2800 K, C_2 absorption profile shows a decrease after reaching maximum concentration. From this measurement, they considered that there must be at least one C_2 formation and one C_2 consumption reaction present and the C_2 consumption reaction was $C_2 + C_2 \leftrightarrow C_3 + C$. Later in 1997 the same group, i.e. Roth et al. first performed quantitative measurement of C, C_2, and C_3 radicals for the study of the kinetics of C_2 radical reactions during the first stage of acetylene high-temperature pyrolysis by monitoring C, C_2, and C_3 radicals[21]. They monitored C_2 absorption in Swan system ($d^3\prod_g \leftarrow a^3\prod_u$) at two deferent wavelengths (467.44 nm and 516.646 nm) and also measured emission spectra of Swan system ($d^3\prod_g \leftarrow a^3\prod_u$, at wavelength >430 nm). C_3 concentration obtained from emission spectra ($A^1\prod_u \leftarrow X^1\sum g^+$) in the spectral range 360-420 nm and Carbon detected at 156.1 nm by ARAS.

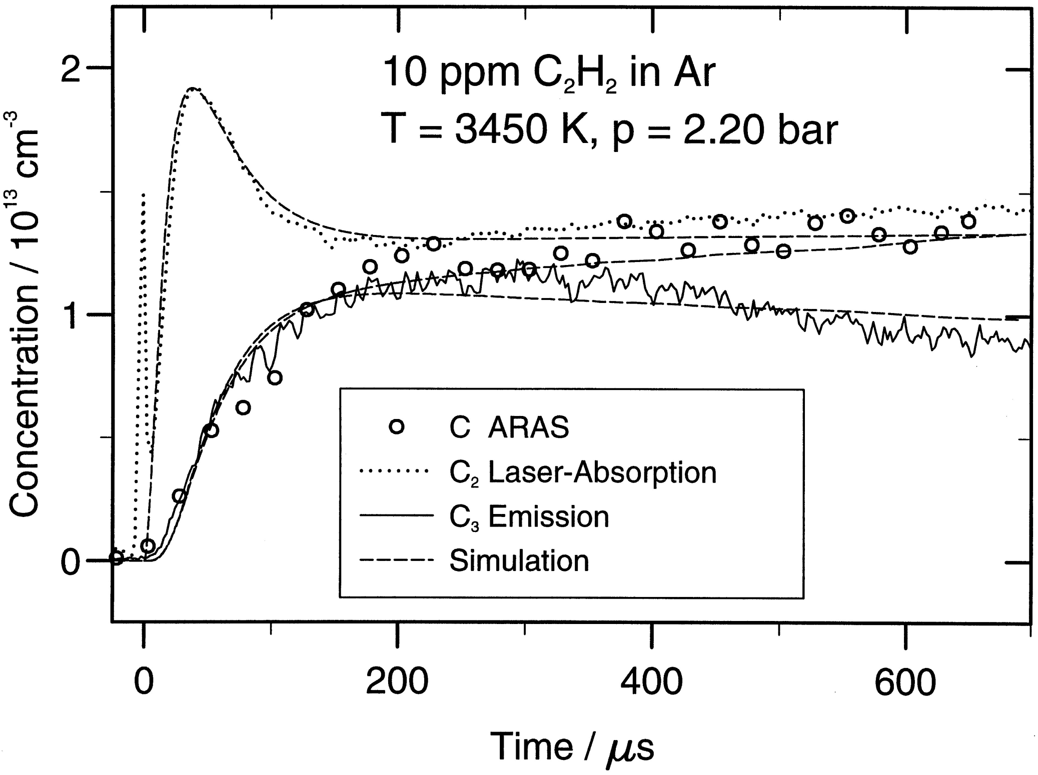


Figure 6.1: Measured and calculated C, C_2, and C_3 concentration during pyrolysis of 10 ppm acetylene diluted in Ar (figure adapted with permission from reference 21. Copyright(1997) American Chemical Society).

They calculated C, C_2, and C_3 concentrations during pyrolysis and plotted C_3 concentration profile along with C_2 and C atom concentration (6.1). Figure 6.1 indicates that a strong formation of both C and C_3 during the time of about 100

μs when the initial C_2 peak decreases to a nearly constant concentration level. So, they concluded that there is a bimolecular reaction:

$$C_2 + C_2 \leftrightarrow C_3 + C$$

and this reaction is one of the important reactions of the pyrolysis of C_2H_2 among the four important reactions. They also included $2C_2 + M \rightarrow C_4$ reaction in their work (reported earlier by Kiefer et al.[19]). Recently our group studied shock-induced thermal processing of C_{60} particle in presence of hydrogen[22]. They found CH_4, C_2H_4, C_2H_2 and C_2H_6 (20.3:7.0:1.7:1.0 ratio) in the post-shock mixture (GC-MS and GC-FID analysis) and lots of carbon particles were also found. But no compound with three carbon atoms was detected and there is a considerable disagreement of experimental result with the kinetic model result (unpublished).

So, it's clear that $C_2 + C_2 \leftrightarrow C_3 + C$ reaction is a very important reaction for pyrolysis of hydrocarbon (like acetylene, ethylene) and is also an important reaction at astrophysical sources (as we mentioned earlier C_2, C_3 and C_5 detected at interstellar medium but still, C_4 is not detected). Till now, very little information is available for this reaction (the rate of different pressure and temperature) and that motivate us to study this reaction. In this work, our key questions will be:

(a) **Does $C_2 + C_2$ really form C_3 or not? And if yes, in which temperature and pressure conditions, formation of C_3 is favourable?**

(b)**As small carbon clusters have low lying excited states, would the different spin states have any importance in these reactions?**

6.2 Computational Details

Potential energy surface calculations are based on all-electron ab initio molecular orbital techniques. MP2(full) method has been used in the determination of molecular geometries. For open-shell species, the spin-unrestricted version of theory and for closed-shell species, the spin-restricted version has been used respectively. For all clusters, geometry was completely optimised with the standard 6-31G(d) basis set. CCSD(T, full) method with cc-pvxz(x=d,t,z) basis set has also been used to optimise the geometry of C_2 and ground state of other pure carbon molecules. In CCSD(T, full) calculations, a closed-shell restricted Hartree-Fock (RHF) reference function has been used for closed-shell species and an unrestricted Hartree-Fock (UHF) reference function has been used for open-shell species. For potential energy surface (along the reaction coordinate) calculation, we used single point energy by CCSD (T, full) method using the geometry obtained by MP2(full) method i.e. CCSD(T, full)/ccpvxz// MP2(full)/6-31G(d) level of theory ('//' indicates the method by which geometries were calculated). Zero-point energies are calculated by HF/6-31G(d) level of theory and scaled by 0.89. All those calculations have been performed with Gaussian 09[23]. CASSCF, CASPT2 and MRCI calculation were done by Molpro[24]. For those calculation we take CASPT2/cc-pvqz geometry. For potential energy surface (along the reaction coordinate) calculation, we used CASSCF(12,12)/ cc-pvqz// CASPT2(12,12)/cc-pvqz, CASPT2(12,12)/ cc-pvqz// CASPT2(12,12)/cc-pvqz and MRCI(12,12)/cc-pvdz // CASPT2(12,12)/cc-pvqz method. For linear C_4 we consider C2v symmetry and for rhombic C_4 we used C1 symmetry.Frequencies are calculated by CCSD (T, full)/cc-pvdz basis set for rate calculations using Gaussian 09.

The rates of all the reactions have been calculated by Multiwell Program Suite. VTST (Variational Transition State Theory) has been used to calculate the rate of the reaction. VTST is the alternative transition state theory in which we can consider the different position for the transition state (trial transition state) along the reaction path and calculate the rate corresponding to each trial transition state. The minimum rate is the rate of that reaction and corresponding trial transition state is the transition state of the reaction. Pressure depended on rate parameter was calculated by muster equation and it calculates time-dependent concentrations and rate constant as a function of pressure and temperature for unimolecular reaction system. For VTST calculations we used ktools code and for muster equation calculation we used muster equation code.

6.3 Results and Discussion

From the previous work, we get the following two types of C_2 addition reactions,

(i) $C_2 + C_2 \leftrightarrow C_3 + C$ i.e., the biradical reaction

(ii) $2C_2 + M \rightarrow C_4$ i.e., unimolecular reaction

Enthalpy of formation of C_4, C_3 and C_2 are 251 kcal/mol, 199 kcal/mol and 195 kcal/mol respectively[8]. Enthalpy of formation of C(triplet) is 169.98 kcal/mol (JANAF thermochemical table). Enthalpy of reaction for $C_2 + C_2 \leftrightarrow C_3 + C$, $\Delta_r H^0$=-21kcal/mol and for $2C_2 + M \rightarrow C_4$, $\Delta_r H^0$=-139 kcal/mol. So, both reactions are exothermic. Two C_2 forming C_4 is an exothermic and highly favourable reaction because in this process new 'C-C' bond is formed. Roth et al.[21] mentioned that $C_2 + C_2 \leftrightarrow C_3 + C$ reaction is a barrierless reaction. But it is turning out to be not true based on our calculation. We did a rigid scan (relax scan is not possible because in that case two C_2 always leads to C_4) by taking two C_2 apart to each other at a distance (3 Angstrom) and then increase C-C bond distance of one C_2 (0.1 Angstrom at each step) and other C_2 remain as it it. This way, $C_2 + C_2$ lead to $C_3 + C$. Quadratic synchronous transit (QST2, QST3) calculation is also not working here because of the same reason i. e. two C_2 is always forming C_4. we did scan for both singlet and triplet surface i.e., $C_2(singlet) + C_2(singlet) \leftrightarrow C_3(singlet) + C(singlet)$ and $C_2(singlet) + C_2(triplet) \leftrightarrow C_3(singlet) + C(triplet)$.

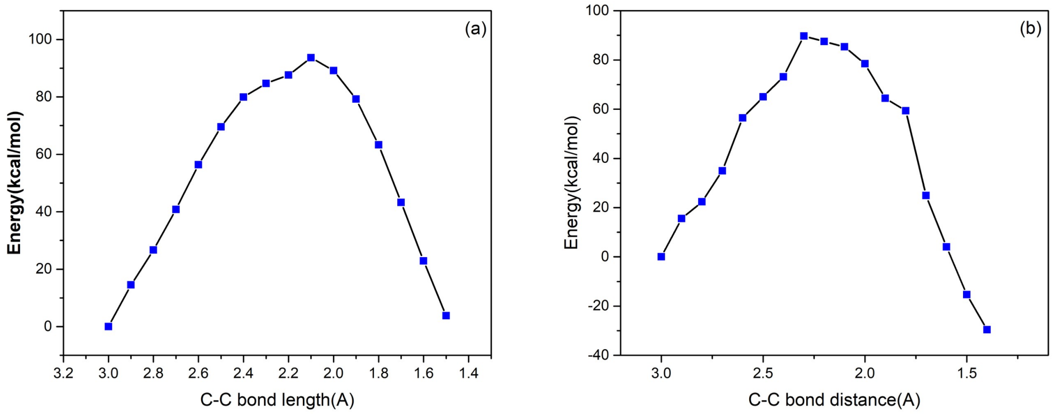


Figure 6.2: Rigid scan (energy: CCSDT/cc-pvqz) including zero-point energy correction (HF/6-31g(d), scaled). (a) $C_2(singlet) + C_2(singlet) \leftrightarrow C_3(singlet) + C(singlet)$; (b) $C_2(singlet) + C_2(triplet) \leftrightarrow C_3(singlet) + C(triplet)$.

Figure 6.2 indicates that $C_2 + C_2 \leftrightarrow C_3 + C$ is not a barrier less reaction and barrier for singlet surface ($\Delta_r H^0$=8 kcal/mol) is 93.64 kcal/mol and for triplet surface ($\Delta_r H^0$=-26 kcal/mol) is 89.74 kcal/mol. But in the reality addition of two C_2 leads to C_3+C may not be a single step process. Two C_2 addition has a high chance to form C_4 which is energetically highly favourable which is expected because the energy of C_4 is more than the sum of energy of two C_2 and from two C_2 addition to C_4 there is a formation of new bond. So here has a strong possibility that two C_2 may not form C_3 in a single step but it can occur via C_4. This kind of reaction is known as **chemical activation reaction**. Chemical activation reaction is a process where a bimolecular recombination reaction (here addition of two C_2) produce an internally energetic species (in this case C_4, which store a lot of energy due to formation of C-C bond by the addition of two C_2) which can subsequently dissociate back along the formation channel (i.e. C_4 dissociate into C_2+ C_2) or dissociate further via other dissociation channel (i.e. C_4 dissociate into C_3+ C)or be stabilized by collision. Figure 6.3 shows the possible chemical activation reaction scheme of two C_2 addition reaction. Two C_2 can form linear C_4. C_4 (linear) which formed by two C_2 addition can further lead to either C_3+C or C_2+C_2 or isomerise to rhombic C_4. Rhombic C_4 can similarly dissociate into C_2+C_2 or cyclic C_3 +C.

The competition between dissociation to either C_3+C or C_2+C_2 will depend on the bond dissociation of C_4. For that in the next section we did rigid scan of the C-

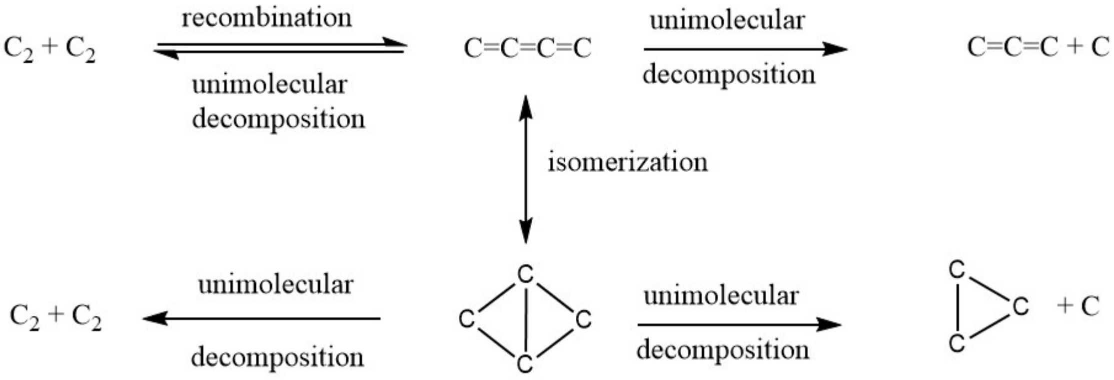


Figure 6.3: Possible chemical activation reaction scheme of two C_2 addition reaction.

C bond of C_4 (both linear and rhombic). As energy difference between singlet and triplet C_2 is less, we consider two case of C_2 addition $(C_2(singlet) + (C_2(singlet)$ and $C_2(singlet) + (C_2(triplet))$. Two singlet C_2 addition leads to singlet C_4 and addition of singlet and triplet C_2 leads to triplet C_4.

6.3.1 Rigid Scan of C-C bond of C_4 (linear/Rhombic)

In this section we discuss rigid scan of C-C bond of C_4. Figure6.4 and 6.6 shows the homolytic dissociation of linear and rhombic respectively C_4 whereas 6.5 and 6.7 shows the hetarolytic dissociation of linear and rhombic C_4 respectively.

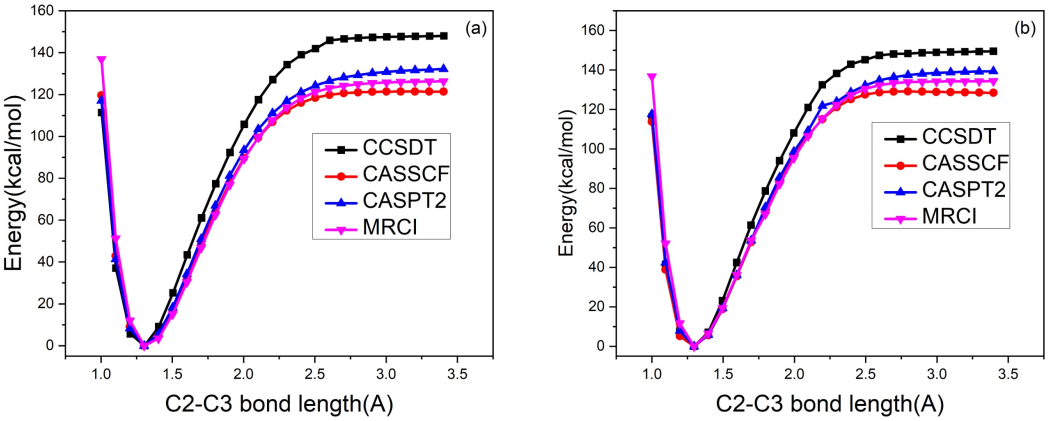


Figure 6.4: Rigid scan of middle C-C bond of (a) singlet and (b) triplet C_4 (linear).

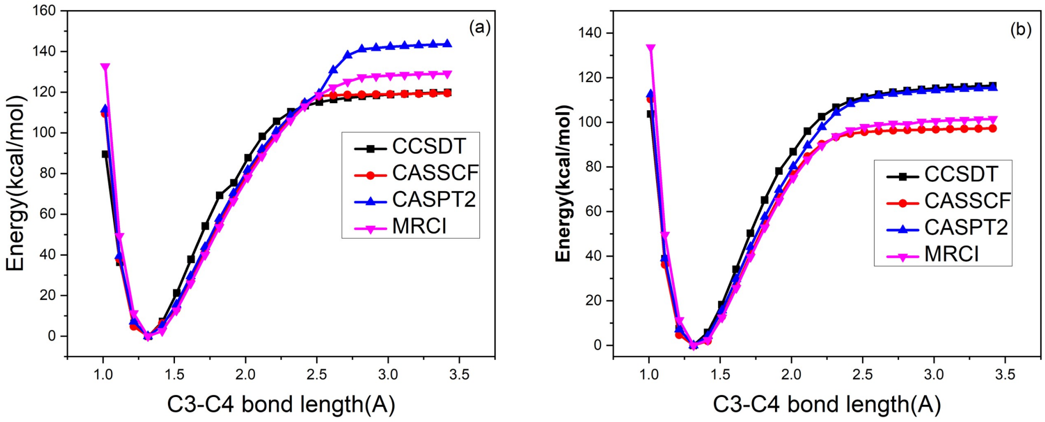


Figure 6.5: Rigid scan of terminal C-C bond of (a) singlet and (b) triplet C_4 (linear).

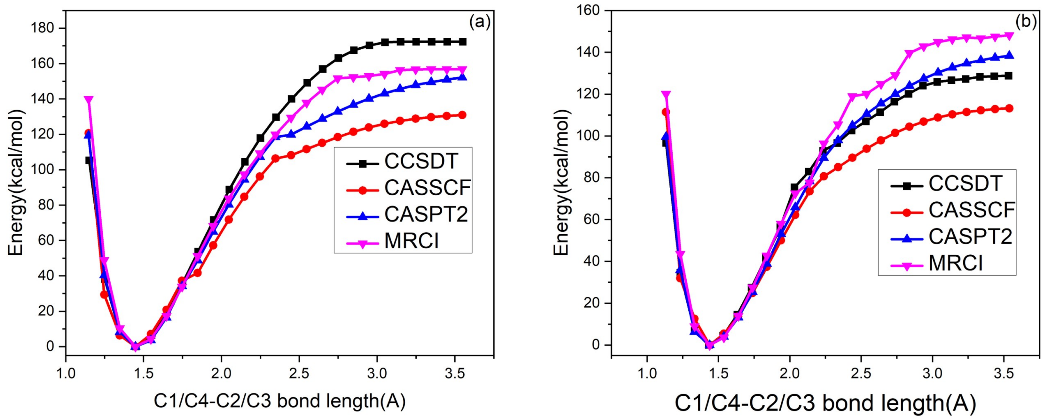


Figure 6.6: Rigid scan of two opposite C-C bond of (a) singlet and (b) triplet C_4 (rhombic).

Those figures clearly indicate that all dissociation channels have no transition state along the reaction path i.e. reverse recombination reactions have no barrier. Singlet cyclic C_3 is transition state of isomerisation of linear C_3, thus cyclic C_3 singlet which is from dissociation of rhombic C_4 is likely going to form linear C_3.

From the table 6.1 we can see that in each level of theory, heterolytic dissociation is more favourable than homolytic dissociation (except CASPT2 method for $linearC_4(singlet) = C(singlet) + C_3(singlet)$ channel). For $linearC_4$, channel 4 i.e. $linearC_4(triplet)toC(triplet)$ & $C_3(singlet)$ is low energy path. For

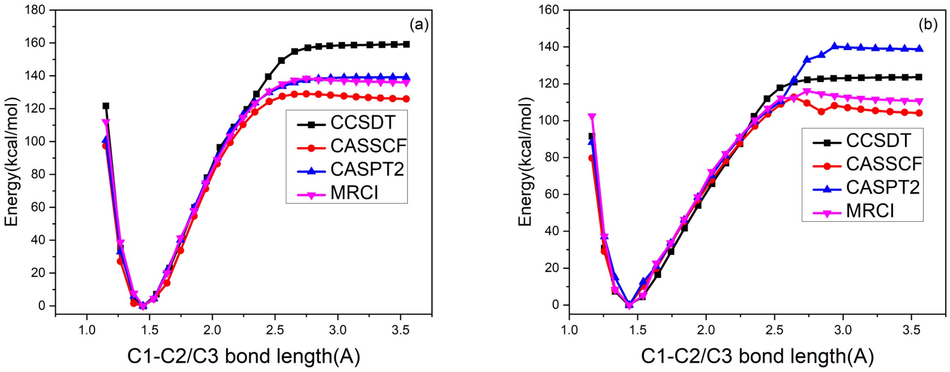


Figure 6.7: Rigid scan of C-C bond of (a) singlet and (b) triplet C_4 (rhombic).

Table 6.1: Comparison of bond dissociation energy of all channel.

Channel	Bond dissociation energy(kcal/mol)			
	CCSDT	CASSCF	CASPT2	MRCI
1. $linearC_4(singlet) = C_2(singlet) + C_2(singlet)$	148.0	121.4	132.2	126.3
2. $linearC_4(singlet) = C(singlet) + C_3(singlet)$	119.9	119.4	143.6	129.2
3. $linearC_4(triplet) = C_2(singlet) + C_2(triplet)$	149.5	128.5	139.4	134.3
4. $linearC_4(triplet) = C(triplet) + C_3(singlet)$	116.4	97.3	115.5	101.5
5. $rhobmicC_4(singlet) = C_2(singlet) + C_2(singlet)$	172.4	130.9	152.1	156.8
6. $rhobmicC_4(singlet) = C(singlet) + cyclicC_3(singlet)$	159.2	125.9	139.2	136.1
7. $rhobmicC_4(triplet) = C_2(singlet) + C_2(triplet)$	128.2	113.2	138.4	148.2
8. $rhobmicC_4(triplet) = C(triplet) + cyclicC_3(singlet)$	123.6	104.2	138.8	110.7

$rhombicC_4$, channel 8 i.e. $rhombicC_4(triplet)$ to $C(triplet)$ & $cyclicC_3(singlet)$ is the low energy path.

6.3.2 Rate calculation of all possible channel

As all the channels have no transition state, we use variational transition state (VST) theory to calculate rate. In VST theory at each point on potential energy surface is taken as a guess transition state. Rate of the reaction is calculated for each guess transition state. Minimum among all rate is taken as the actual rate of the reaction. Harmonic vibrational frequency calculation done for each point along the reaction coordinate (guesses transition state) by CCSD(T,full)/ccpvdz method. In few guesses transition state, there present more than one (usually two) negative frequency. For that case we change the geometry along that coordinate manually, repeat the frequency analysis, repeat this process until there are no more than one negative frequency. Finally, we consider all frequency as harmonic oscillator in our calculation.

6.3.2.1 Rate of $C_4 \leftrightarrow C_3 + C/C_2 + C_2$ reactions (rate by VST)

Figure 6.8, Figure 6.9, Figure 6.10 and Figure 6.11 show the rate of unimolecular decomposition of C_4 (linear and rhombic) at different levels of theory. For linear

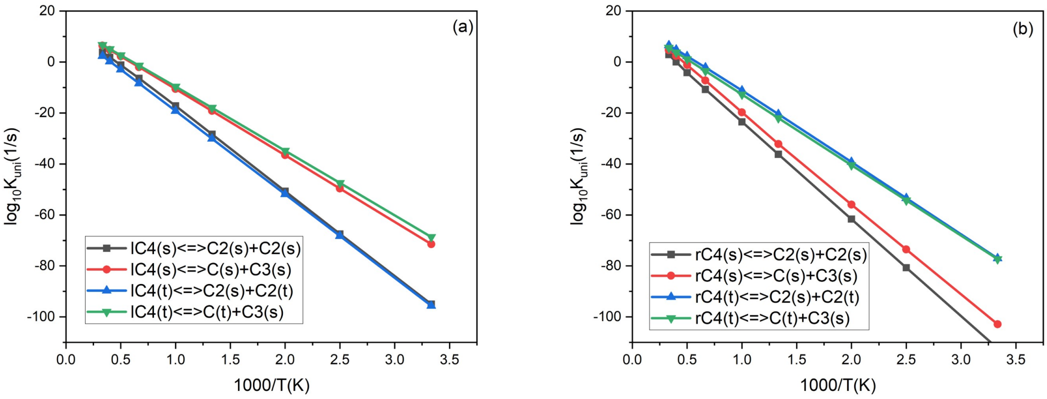


Figure 6.8: Rate of unimolecular decomposition of C_4 (linear/rhombic) at CCSDT level of theory. (a) decomposition of $linearC_4$ and (b) decomposition of $rhombicC_4$.

C_4 there are four different dissociation channels:

(i) $linearC_4(singlet)$ dissociate to $C_2(singlet)$ and $C_2(singlet)$ ($lC_4(s) \leftrightarrow C_2(s) + C_2(s)$)

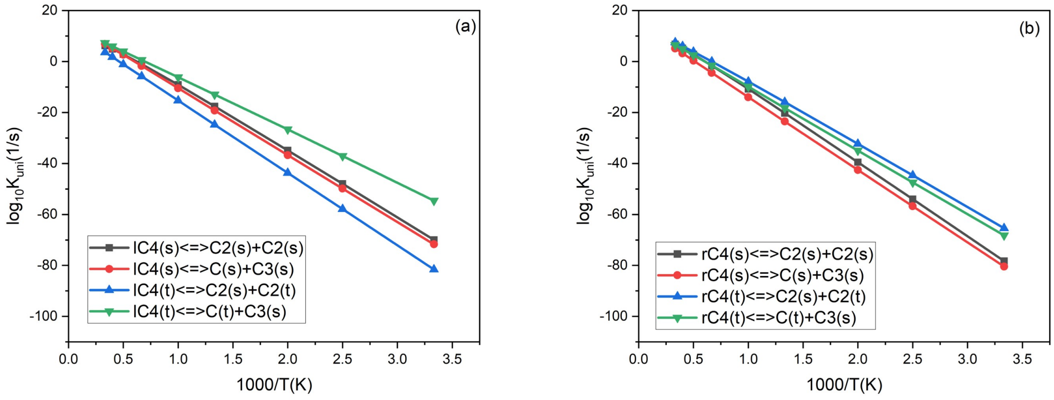


Figure 6.9: Rate of unimolecular decomposition of C_4 (linear/rhombic) at CASSCF level of theory. (a) decomposition of $linearC_4$ and (b) decomposition of $rhombicC_4$.

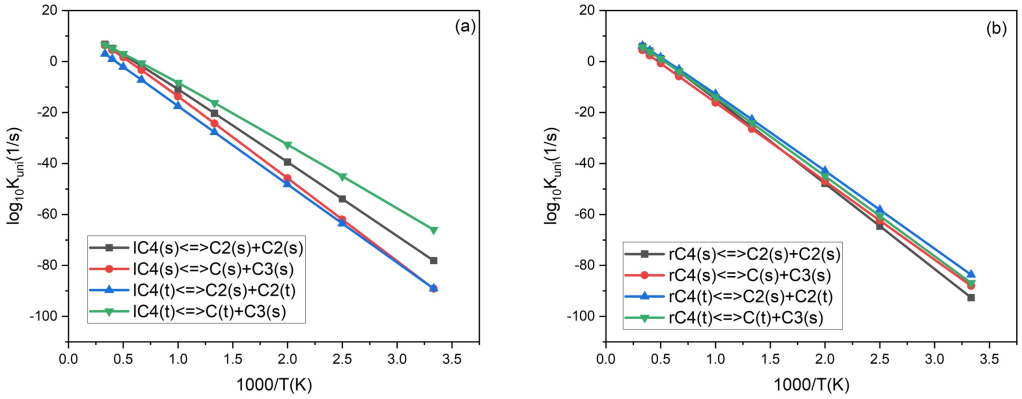


Figure 6.10: Rate of unimolecular decomposition of C_4 (linear/rhombic) at CASPT2 level of theory. (a) decomposition of $linearC_4$ and (b) decomposition of $rhombicC_4$.

(ii) $linearC_4(singlet)$ dissociate to $C_3(singlet)$and $C(singlet)$ ($lC4(s) \leftrightarrow C_3(s)+C(s)$)

(iii) $linearC_4(triplet)$ dissociate to $C_2(singlet)$ and $C_2(triplet)$ ($lC4(t) \leftrightarrow C2(s)+C2(t)$)

(iv) $linearC_4(triplet)$ dissociate to $C_3(singlet)$and $C(triplet)$ ($lC4(t) \leftrightarrow C3(s)+C(t)$)

Similarly, for rhombic C_4 there are four different dissociation channels:

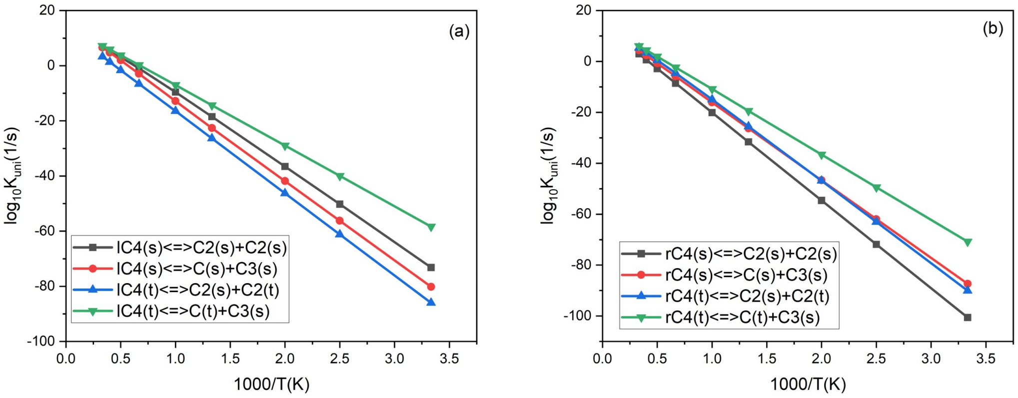


Figure 6.11: Rate of unimolecular decomposition of C_4 (linear/rhombic) at MRCI level of theory. (a) decomposition of $linearC_4$ and (b) decomposition of $rhombicC_4$.

(v) $rhombicC_4(singlet)$ dissociate to $C_2(singlet)$ and $C_2(singlet)$ $(rC4(s) \leftrightarrow C2(s) + C2(s))$

(vi) $rhombicC_4(singlet)$ dissociate to $C_3(singlet)$ and $C(singlet)$ $(rC4(s) \leftrightarrow C3(s) + C(s))$

(vii) $rhombicC_4(triplet)$ dissociate to $C_2(singlet)$ and $C_2(triplet)$ $(rC4(t) <=> C2(s) + C2(t))$

(viii) $rhombicC_4(triplet)$ dissociate to $C_3(singlet)$ and $C(triplet)$ $(rC4(t) <=> C3(s) + C(t))$

From the figure we can see that among the dissociate channel of $linearC_4$, rate constant of dissociation of triplet C_4 into singlet C_3 and triplet C (channel 4) is the highest across four different levels of theory. Triplet C_4 dissociating into singlet C_2 and triplet C_2 (channel 3) is the slowest process in all the levels of theory. Rate constant of dissociation of singlet C_4 vary at different levels of theory. At CCSDT level of theory rate of dissociation of singlet C_4 into singlet C_3 and singlet C is faster than the dissociation into singlet C_2 and singlet C_2. But at CASSCF, CASPT2 and MRCI level of theory, rate constant of dissociation of singlet C_4 into two singlet C_2 is faster than dissociating into singlet C_3 and Singlet C.

Dissociation of $rhombicC_4$ significantly deviate at different levels of theory. Dissociation of rhombic triplet C_4 into singlet C_2 and triplet C_2 is the fastest process at CCSDT, CASSCF and CASPT2 level of theory whereas rhombic triplet C_4 dissociate into singlet C_3 and triplet C is the fastest process at MRCI level of theory. Dissociation of rhombic singlet C_4 into two singlet C_2 is the slowest process at CCSDT, CASPT2 and MRCI level of theory whereas rhombic singlet C_4 dissociate into singlet C_3 and singlet C is the slowest process at CASSCF level of theory.

Figure 6.12, figure 6.13, figure 6.14 and figure 6.15 show the rate of recombination reaction of above mention eight channels.

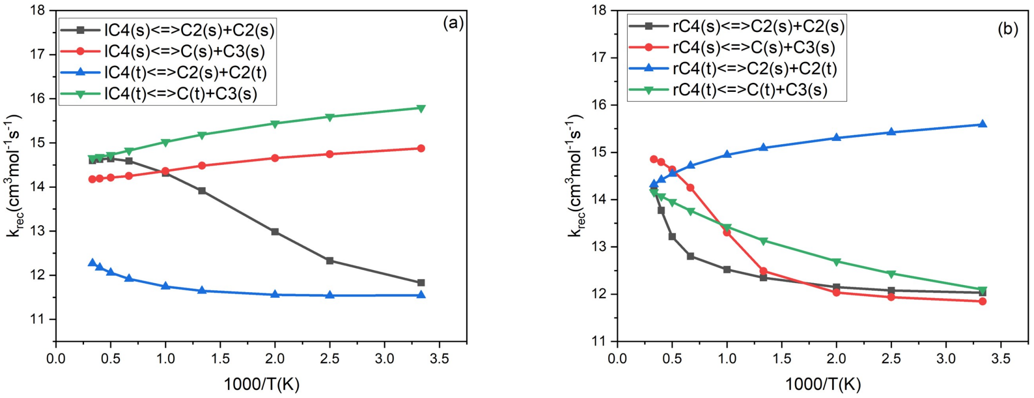


Figure 6.12: Rate of bimolecular recombination reaction to form $C_4(linear/rhombic)$ at CCSDT level of theory. (a) recombination leads to $linear C_4$ and (b) recombination leads to $rhombic C_4$.

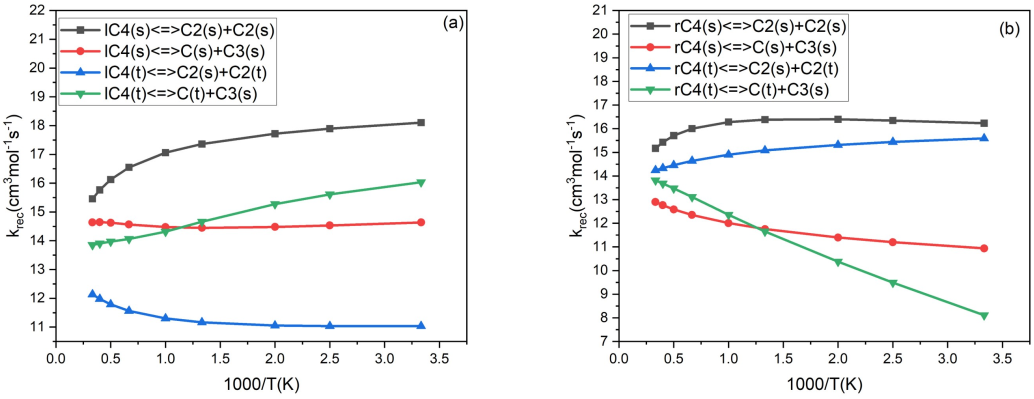


Figure 6.13: Rate of bimolecular recombination reaction to form $C_4(linear/rhombic)$ at CASSCF level of theory. (a) recombination leads to $linear C_4$ and (b) recombination leads to $rhombic C_4$.

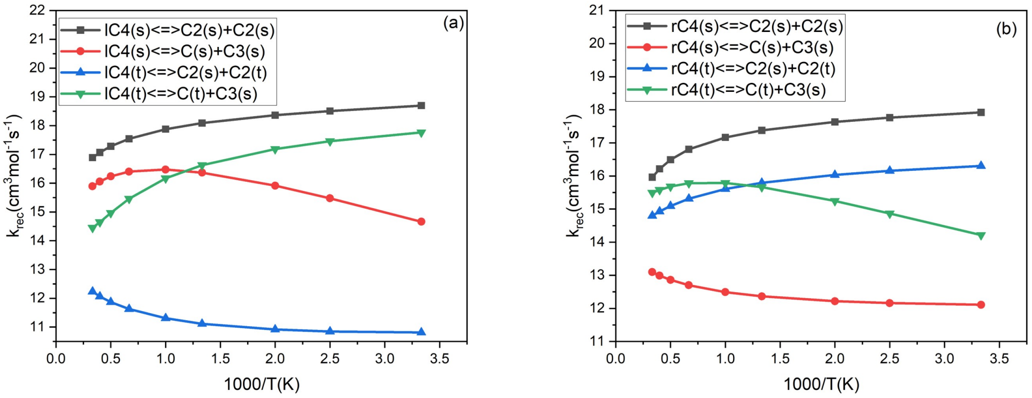


Figure 6.14: Rate of bimolecular recombination reaction to form $C_4(linear/rhombic)$ at CASPT2 level of theory. (a) recombination leads to $linearC_4$ and (b) recombination leads to $rhombicC_4$.

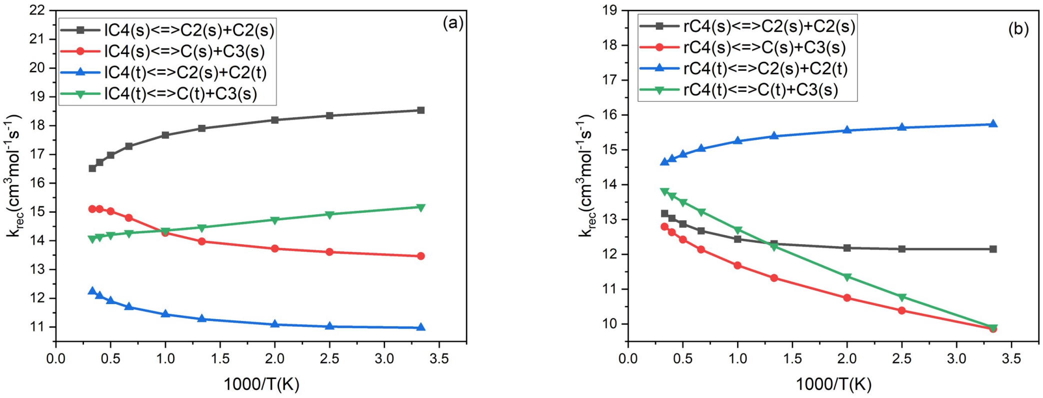


Figure 6.15: Rate of bimolecular recombination reaction to form $C_4(linear/rhombic)$ at MRCI level of theory. (a) recombination leads to $linearC_4$ and (b) recombination leads to $rhombicC_4$.

For $linearC_4$, across the level of theory, rate of formation of triplet by recombination of triplet C_2 and singlet C_2 is slowest process. At CCSDT level of theory formation of triplet C_4 by recombination of singlet C_3 and triplet C is the fastest process at low temperature whereas as temperature increases the rate of formation of singlet C_4 by recombination of two singlet C_2 increases and it becomes the fastest process. At CASSCF, CASPT2 and MRCI level of theory, rate of formation of singlet C_4 by recombination of two singlet C_2 is the fastest process. For

$rhombicC_4$ formation, there is no clear trend and its highly dependent on the level of theory. It is clear from those values that triplet $linearC_4$ prefers to dissociate into singlet C_3 and triplet C at all levels of theory. However, for singlet $linearC_4$, at some level of theory dissociation into two singlet C_2 is fastest while at another level of theory, dissociation into two C_2 singlet is preferable.

6.3.2.2 Rate by Master Equation Code

To incorporate pressure dependency in rate, we used Multiwell Master Equation Code. Here we take Argon as a collider, Biexponential model as a collision model. Here two parameters we consider:

a) *Lennard-Jones(LJ) parameters:* As no experimental data of LJ parameters for linear and rhombic C_4 is available , so we consider LJ value of C_3H_6 for $linearC_4$ and LJ value of $c - C_3H_6$ for $rhombicC_4$.

b) *Energy transfer parameter α, exponential down model:* Most of the case parameter α in the exponential model (single component of the bi-exponential model) is in the range from 100 cm^{-1} to 1000 cm^{-1}. We take 250 cm^{-1} as α value.

In this calculation, we consider all dissociation channel of linear and rhombic C_4 and consider isomerisation between $linearC_4$ to $rhombicC_4$ (Figure 6.3). Blanksby et al.[25] did both experimental and theoretical Study of conversion of linear to rhombic C_4 in the gas phase. We repeated the calculation for conversion of linear to rhombic C_4 and used activation energy of isomerisation for our muster code simulation. Rate of $C_2 + C_2 \leftrightarrow lC_4/rC_4 \rightarrow C_3 + C$ reaction is calculated by the following formula:

$$k_{(C_2+C_2 \rightarrow C_3+C)}(T, [M]) = k_{rec}\infty(T) \times f(D, \infty)$$

where $k_{rec}\infty(T)$ is the high-pressure limit for $C_2 + C_2$ recombination reaction and $f(D, \infty)$ is fraction of $C_3 + C$.

For all the methods, $C_2 + C_2 \leftrightarrow lC_4/rC_4 \rightarrow C_3 + C$ at triplet surface give predominantly C_3 whereas formation of C_2 is very less amount at mainly high temperature. C_4 mainly forms at the temperature less than 500K and high pressure (100 bar). There is no significant dependence on pressure beyond temperature more than 500K at triplet surface. On the other hand, at the singlet surface C_2 mainly formed at high temperature and there is pressure dependency all over the temperature. C_4 mainly formed at low temperature (<500 K) and high pressure (>10 bar).

We observed almost negligible amount of $rhombicC_4$ at all the level of theory. Although due to the higher density of states of the linear isomers, resulting from their low bending frequencies, these species possess higher entropies of formation[25,26] and for that reason linear isomers may be formed more readily, (e.g.,

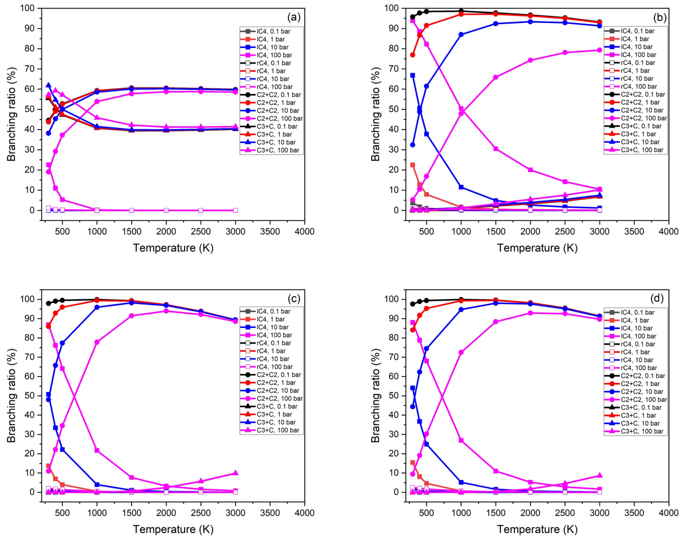


Figure 6.16: Calculated branching ratios as the function of temperature of temperature and pressure at the singlet surface.(a) CCSDT method, (b) CASSCF method, (c) CASPT2 method and (d) MRCI method.

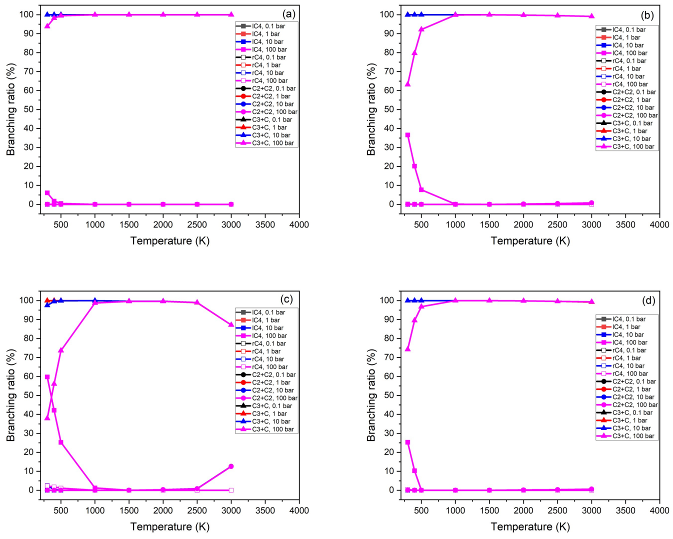


Figure 6.17: Calculated branching ratios as the function of temperature of temperature and pressure at the triplet surface.(a) CCSDT method, (b) CASSCF method, (c) CASPT2 method and (d) MRCI method.

Slanina[26] estimated that the rhombic isomer of C_4 would account for no more than 10% of the C_4 clusters present in the vapor at equilibrium, based on theoretical calculations).

As we mention earlier that two C_2 addition to forming C_4 is energetically highly favourable as it is exothermic reaction and also it is barrier less reaction and, in this process, C_4 store lots of energy. C_4 can spend its energy either by collision or dissociation. So in high-pressure region C_4 is stabilized by collision with other molecule. But in low-pressure region C_4 dissociates (disproportionation reaction) to form $C_3 + C$, or undergoes homolytic dissociation to form two C_2.

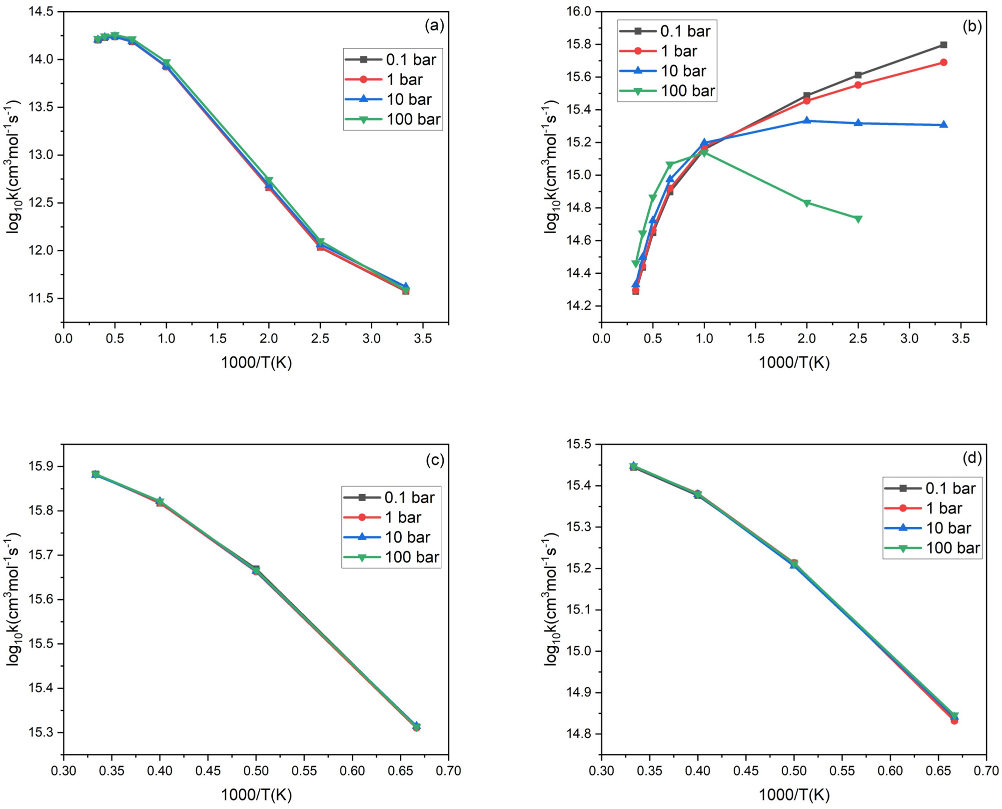


Figure 6.18: Rate constant ($k = k_{(C_2+C_2 \rightarrow C_3+C)}$) for the $C_2 + C_2 \rightarrow C_3 + C$ reaction at singlet surface as a function of temperature and pressure. (a) CCSDT method, (b) CASSCF method, (c) CASPT2 method and (d) MRCI method

In combustion system both temperature and pressure are usually very high, i.e. temperature range is 1000-3000 K and pressure range is 1-10 bar. In our master code simulation, we can see that at temperature above 500 K, addition of C_2 forming mainly C_3 and C as a result of complete dissociation of $linearC_4$

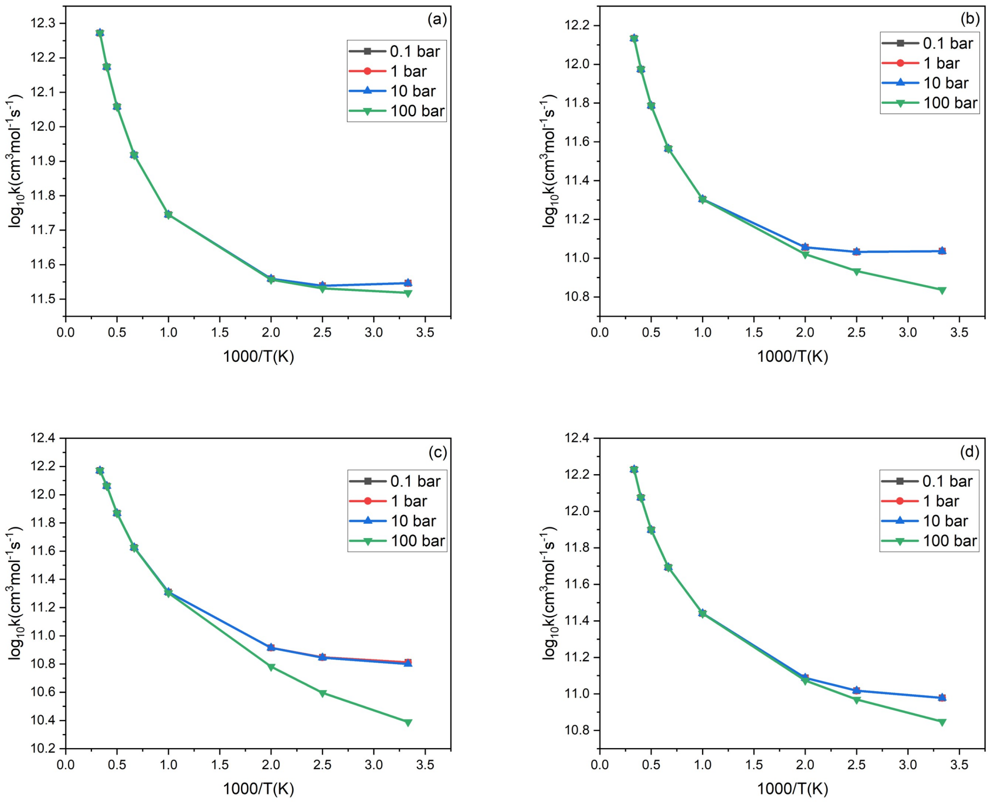


Figure 6.19: Rate constant ($k = k_{(C_2+C_2\rightarrow C_3+C)}$) for the $C_2+C_2 \rightarrow C_3+C$ reaction at triplet surface as a function of temperature and pressure. (a) CCSDT method, (b) CASSCF method, (c) CASPT2 method and (d) MRCI method

mainly at triplet surface and pressure has very little effect in that temperature range whereas addition of C_2 leading to C_2 via $linear C_4$ at singlet surface.

6.4 Conclusion

Some conclusions can be reached based on the present theoretical investigation. $C_2+C_2 \leftrightarrow C_3+C$ is not a barrierless reaction and it is unlikely that it is a one-step reaction. C_2 addition reaction occurs via C_4 i.e. $C_2+C_2 \leftrightarrow C_4 \rightarrow C_3+C$ and it is a good examples of chemical activation reaction. Less than 500 K temperature and high pressure (pressure more than 10 bar) C_4 mainly from by addition of C_2 mainly at singlet surface. At temperature more than 500 K, C_2 mainly form at singlet surface whereas C_3+C form at triplet surface. $C_2+C_2 \leftrightarrow C_4 \rightarrow C_3+C$ reaction is sensitive to spin state of C_2 and $C_2 + C_2 \to C_3 + C$ reaction ($k_{C_2+C_2\to C_3+C}$) at singlet surface is faster than that in triplet surface (based on master equation rate calculation, figure 6.18 and figure 6.19). Formation of cyclic carbon species (i.e. $rhombicC_4$) is negligible in our calculation, so cyclic species may not be important in $C_2 + C_2 \leftrightarrow C_4 \to C_3 + C$ reaction.

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6.5 Supplementary Information

6.5.1 Energy and bond length of C_2, C_3 and C_4 at verious level of theory

Table 6.2: Energy and bond length of carbon species

Molecule	Spin State	Level of Theory	Energy (Hartree)	ZPE (kcal/mol)	Harmonic Frequency (cm^{-1})	Bond Length (A)
C_2	Singlet	HF/6-31g(d)	-75.3790284	2.77	1940	1.245
		MP2-F/6-31g(d)	-75.704617	2.73	1909	1.264
		CCSDT-F/cc-pvqz	-75.855232	2.67	1869	1.242
		CCSDT-F/cc-pvqz //MP2-F/6-31G(d)	-75.854587			
		CASSCF(8,8)/cc-pvqz	-75.64334257			1.254
		CASPT2(8,8)/cc-pvqz	-75.79328770			1.247
		MRCI(8,8)/cc-pvdz	-75.72611707			1.272
		Expt		2.65	1855.7	1.243
	Triplet	HF/6-31g(d)	-75.472004	2.6	1822	1.292
		MP2-F/6-31g(d)	-75.69469	2.4	1682	1.321
		CCSD(T)/cc-pvdzb	-75.72528	2.31	1615	1.34
		CCSD(T,Full)/cc-pvqz	-75.848832	2.41	1688	1.307
		CCSDT-F/cc-pvqz //MP2-F/6-31G(d)	-75.851088			
		CASSCF(8,8)/cc-pvqz	-75.62540264			1.328
		CASPT2(8,8)/cc-pvqz	-75.78893866			1.318
		MRCI(8,8)/cc-pvdz	-75.72386941			1.342
		Expt		2.35	1641	1.312

Molecule	Spin State	Level of Theory	Energy (Hartree)	ZPE (kcal/mol)	Harmonic Frequency (cm^{-1})	Bond Length (A)
C_3 *linear*	Singlet	HF/6-31g(d)	-113.3551011	5.67	153(2),1367 ,2312	1.277
		MP2-F/6-31g(d)	-113.7056456	5.41	190(2),1220 ,2184	1.302
		CCSDT-F/cc-pvqz	-113.9437073	5.01	86(2),1213, 2116	1.294
		CCSDT-F/cc-pvqz //MP2-F/6-31G(d)	-113.9435408			
		CASSCF(8,8)/cc-pvqz	-113.51915990			1.288
		CASPT2(8,8)/cc-pvqz	-113.83451602			1.297
		MRCI(8,8)/cc-pvdz	-113.72358750			1.315
		Expt		4.85	63.4, 1227, 2040	1.297
	Triplet	HF/6-31g(d)	-113.2605046	4.83	115, 319, 1196, 1748	1.3
		MP2-F/6-31g(d)	-113.6230266	6.63	320, 483, 1331, 2500	1.289
		CCSDT-F/cc-pvqz //MP2-F/6-31G(d)	-113.8550402			
		CASSCF(8,8)/cc-pvqz	-113.43644486			1.295
		CASPT2(8,8)/cc-pvqz	-113.76823373			1.305
		MRCI(8,8)/cc-pvdz	-113.62215732			1.317

Molecule	Spin State	Level of Theory	Energy (Hartree)	ZPE (kcal /mol)	Harmonic Frequency (cm^{-1})	Bond Length (A)
C_3 *cyclic*	Singlet	HF/6-31g(d)	-113.2986792	4.79	-1403, 1340, 2012	R12=1.461 R23=1.250
		MP2-F/6-31g(d)	-113.6650975	4.47	-1324, 1305, 1823	R12=1.460 R23=1.279
		CCSDT-F/cc-pvqz //MP2-F/6-31g(d)	-113.903719			
		CASSCF(8,8)/cc-pvqz	-113.37749988			R12=1.465 R23=1.245
		CASPT2(8,8)/cc-pvqz	-113.80658145			R12=1.457 R23=1.269
		MRCI(8,8)/cc-pvdz	-113.64668856			R12=1.482 R23=1.280
	Triplet	HF/6-31g(d)	-113.326372	5.65	1090(2), 1773	1.346
		MP2-F/6-31g(d)	-113.685756	95.15	1609(2), 32475	1.386
		CCSDT-F/cc-pvqz	-113.913042	5.76	1223, 1232, 1578	1.372
		CCSDT-F/cc-pvqz //MP2-F/6-31g(d)	-113.912654			
		CASSCF(8,8)/cc-pvqz	-113.45327592			1.373
		CASPT2(8,8)/cc-pvqz	-113.80345419			1.365
		MRCI(8,8)/cc-pvdz	-113.78352536			1.365

Molecule	Spin State	Level of Theory	Energy (Hartree)	ZPE (kcal /mol)	Harmonic Frequency (cm^{-1})	Bond Length (A)
C_4	Triplet	HF/6-31g(d)	-151.1837241	9.07	210(2),408(2), 1021,1740,2345	R12=1.299, R23=1.276
linear		MP2-F/6-31g(d)	-151.6100253	8.43	181(2),401(2), 935,1563,2128	R12=1.312, R23=1.296
		CCSDT-F/cc-pvqz	-151.9399317	8.21	174(2),373(2), 934,1588,2123	R12=1.309, R23=1.289
		CCSDT-F/cc-pvqz //MP2-F/6-31G(d)	-151.9398389			
		CASSCF(12,12) /cc-pvqz	-151.3825216			R12=1.304 R23=1.300
		CASPT2(12,12) /cc-pvqz	-151.8040257			R12=1.314 R23=1.296
	Expt				1548.9, 2032	
	Singlet	HF/6-31g(d)	-151.1355998	9.21	217, 218, 427, 474,1025, 1740, 2341	R12=1.296 R23=1.281
		MP2-F/6-31g(d)	-151.5957361	8.26	169, 202, 372, 413,926, 1586, 2110	R12=1.318 R23=1.305
		CCSDT-F/cc-pvqz //MP2-F/6-31G(d)	-151.9258127			
		CASSCF(12,12) /cc-pvqz	-151.3715449			R12=1.306 R23=1.309
		CASPT2(12,12) /cc-pvqz	-151.7928917			R12=1.316 R23=1.303

Molecule	Spin State	Level of Theory	Energy (Hartree)	ZPE (kcal /mol)	Harmonic Frequency (cm^{-1})	Bond Length (A)
C_4 *rhombic*	Singlet	HF/6-31g(d)	-151.1459789	8.57	351, 450, 1088, 1103, 1432, 1569	R12=1.425 R24=1.457
		MP2-F/6-31g(d)	-151.6347291	8.37	374, 713, 950,1103, 1285,1429	R12=1.451 R24=1.523
		CCSDT-F/cc-pvqz	-151.9405508	7.88	303, 540, 951, 1044, 1275, 1400	R12=1.444 R24=1.505
		CCSDT-F/cc-pvqz //MP2-F/631g(d)	-151.9395289			
		CASSCF(12,12) /cc-pvqz	-151.3573380			R12=1.436 R24=1.532
		CASPT2(12,12) /cc-pvqz	-151.79694376			R12=1.448 R24=1.513
	Triplet	HF/6-31g(d)	-151.0854964	8.18	533, 506, 671, 1093, 1562, 1890	R12=1.411 R24=1.398
		MP2-F/6-31g(d)	-151.6056879	11.27	621, 723, 877, 1316, 1339, 3004	R12=1.433 R24=1.595
		CCSDT-F/cc-pvqz //MP2-F/6-31g(d)	-151.901789			
		CASSCF(12,12) /cc-pvqz	-151.32036299			R12=1.433 R24=1.617
		CASPT2(12,12) /cc-pvqz	-151.77658937			R12=1.439 R24=1.597

Chapter 7

Conclusions

In this thesis, the pyrolysis of iso-propylcyclohexane, and 1,3,5-trimethylcyclohexane have been investigated by shock tube experiments. Thermal decomposition of iso-propylcyclohexane, 1,3,5-trimethylcyclohexane, and decalin have been investigated theoritically (quantum chemistry calculations). We also investigated $C_2 + C_2$ reaction computationally. The kinetic model for the high temperature, high pressure pyrolysis of iso-propylcyclohexane, and 1,3,5-trimethylcyclohexane have been developted from experimental observation, theoritical calculation, and literature review; model has been validated aginest experimental data. For decalin, we calculated high pressure rate paremeter for all important elimentary reaction of thermal decompositon which can help to build kinetic model.For $C_2 + C_2$ reaction, we have calculated pressure-dependent rate parameters to determine the temperature and pressure conditions in which $C_2 + C_2$ leads to $C_3 + C$.

The main conclusions from theoritical study are as follows:

(1) The initial decomposition of iso-propylcyclohexane is the side-chain isopropyl group elimination followed by side-chain CH_3 group elimination. H-abstraction reaction barrier for IPCH is more than H-abstraction reaction in methylcyclohexane. For ring-opening isomerization of IPCH radical, C-C bond dissociation adjacent to the iso-propyl group has a lower energy barrier than the other IPCH radical, which is a similar trend for MCH radical and ECH radical as well. Alkenyl radicals are obtained by opening the ring of IPCH radical. These alkenyl radicals then either isomerize to cyclopentane radical or isomerized to other alkenyl radicals by intramolecular H-migration or dissociate. Cyclopentadiene, methylcyclopentadiene, benzene, and styrene can be formed by stepwise dehydrogenation of cyclic intermediates. Stepwise dehydrogenation of iso-propylcyclohexene are energetically favorable than that of similar stepwise dehydrogenation of cyclohexene.

(2) For 1,3,5-trimethylcyclohexane, rate constant of methyl-loss channel is more than ring-opening isomerization. For trans-1,3,5-trimethylcyclohexane, rate constant of axial methyl-loss channel is more than equatorial methyl-loss channel.

Rate constant of H-abstraction reaction for cis-1,3,5-trimethylcyclohexane is higher than trans-1,3,5-trimethylcyclohexane. Cyclopentadiene, methylcyclopentadiene, benzene, and toluene are formed by stepwise dehydrogenation of cyclic intermediates. Stepwise dehydrogenation of 1,3,5-trimethylcyclohexane are energetically favourable than that of similar stepwise dehydrogenation of cyclohexene.

(3) For decalin, our calculations show that the initial decomposition channel is the ring-opening channel rather than C-H dissociation channel. Energy barrier of H-abstraction reaction of decalin is comparable with methylcyclohexane. We proposed reaction mechanism of arometic products like benzene, toulene, styrene, o-xylene, tetralin, and naphthalene formation which are experimentally detected by verious groups, from results avalable in literature.

(4) Energy barrier of C-H dissociation of decalin is higher than that of cyclohexane. Among methylcyclohexane, iso-propylcyclohexane and 1,3,5-trimethylcyclohexane, energy barrier for CH_3 elimination is least for trans-1,3,5-trimethylcyclohexane (axial group CH_3 elimination) followed by iso-propylcyclohexane. Among cyclohexane, methylcyclohexane, iso-propylcyclohexane and 1,3,5-trimethylcyclohexane, and decalin, energy barrier of ring-opening of decalin is least followed by methylcyclohexane.

(5)Our calculation shows that the $C_2 + C_2$ reaction leading to $C_3 + C$, is not a barrier-less reaction, and it occurs via C_4 intermediate.Less than 500 K temperature and high pressure (pressure more than 10 bar) C_4 formation by addition of two C_2 dominates reaction in singlet surface. At a temperature of more than 500 K, reverse reaction of C_4 leading to C_2 dominates the reaction in singlet surface. However, formation of $C_3 + C$ dominates reaction at the triplet surface. Thus, $C_2 + C_2 \leftrightarrow C_4 \rightarrow C_3 + C$ reaction is sensitive to the spin state of C_2, and $C_2 + C_2 \rightarrow C_3 + C$ reaction at singlet surface is faster than that on triplet state.

The main conclusions from experimental study are as follows:

(1) The shock tube pyrolysis experiments of iso-propylcyclohexane have been carried out for temperatures ranging from 923-1526 K and pressure ranging from 9.8–20.2 bar. Concentrations of all the major and minor products have been measured using GC-FID and GC-MS. The major products observed in the post shock mixture have been the following: methane, ethene, acetylene, ethane, propene, allene, propyne, vinylacetylene, 1,3-butadiene, pentadiene, cyclopentadiene, and benzene. The minor products are the following: propane, butene, 1,3-butadiyne, butyne, methylbutadiene, methylpentadiene, methylcyclopentadiene, cyclohexadiene, cyclohexene, toluene, styrene, and ethylidenecyclohexane. Ethene is the most abundant product. Experimental measurements have been used to validate the kinetic mechanism proposed in the theoretical study.

(2) The shock tube pyrolysis experiments of 1,3,5-trimethylcyclohexane have

been carried out for temperatures ranging from 1017- 1542 K and pressure ranging from 13.35–23.46 bar. The major products observed in the post-shocked mixture have been the following: methane, ethene, acetylene, ethane, propene, allene, propyne, 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, cyclopentadiene, and benzene. The minor products observed are the following: vinylacetylene, toluene, butene, 1,3-butadiyne, butyne, methylbutadiene, 3-methylpentadiene, 2-methylpentadiene, 5-methylcyclopentadiene, 1-methylcyclopentadiene, cyclohexadiene, 1,3-dimethyl-cyclohexane-cis, 1,3-dimethylcyclohexane-trans, styrene, 3,3,5-trimethylcyclohexane, 1,2,4-trimethylcyclohexane, and 1-ethyl,1-methylcyclohexane. Methane is the most abundant product. Experimental measurements have been used to validate the kinetic mechanism proposed in the theoretical study.

(3) Both MCH and 135TCH start dissociating around 1100 K whereas IPCH starts dissociating at 1050 K. Among the products from pyrolysis, both 135TCH and IPCH produce many branched species which are absent during MCH pyrolysis. The pyrolysis of 135TCH/IPCH produces branched unsaturated species like, methylpentadiene, methylbutadiene, methylcyclopentadiene which have not been reported during the pyrolysis of MCH.

The main conclusions from kinetic modeling follow:

(1) The initial consumption of iso-propylcyclohexane mainly done by H-abstraction reaction followed by unimolecular decomposition reactions. Ring-opening isomerization channel has negligible contribution (1.2%) on initial compumtion. The most sensitive reaction of iso-propylcyclohexane consumption has been the dissociation of iso-propylcyclohexane to isopropyl radical and cyclohexyl radical. Step-wise dehydrogenation of cyclic intermediate has less effect (11%) towards benzene formation. Benzene maily formed by addition of resonance stabilized intermediate/radical(propargyl radical, allene, propyne, etc.).Cyclohexyl radical (cC_6H_{11}) plays a key role in forming aromatic products (benzene, toluene, and styrene).

(2) The initial consumption of 1,3,5-trimethylcyclohexane mainly done by H-abstraction reaction followed by unimolecular decomposition reactions. Ring-opening isomerization channel has negligible contribution (2.3%) on initial consumption. The most sensitive reaction of 1,3,5-trimethylcyclohexane consumption has been the CH_3 elimination channel. Benzene mainly formed by addition of resonance stabilized intermediate/radical and step-wise dehydrogenation of cyclic intermediate has no effects on it. Allene and dimethylcyclohexane radicals play key roles in the formations of aromatic products (benzene, toluene, and styrene).

Appendices

Appendix A

Development of a sensor for calculating temperature and water concentration in combustion gases using a single tunable diode laser

A.1 Introduction

Combustion is the most widely used energy conversion technique in the world. Measurements of important combustion parameters such as temperature and species concentration are essential to understand the combustion processes, to improve the combustion efficiency and to reduce the production of pollutants.

Till today in our laboratory we study combustion/pyrolysis of various fuel to understand kinetics of their decomposition using shock tube at various temperature (900-1600 K) and pressure (9-25 bar). We calculate temperature using chemical thermometry and there is no way to calculate concentration of major combustion species like water, CO_2, CO, NO etc.

Diode laser absorption sensors offers significant opportunities and advantages for in situ measurements of temperature and concentration of major combustion species due to their high sensitivity, high spectral resolution and fast time response[1–3]. We can measure temperature by two colors method based on Beer-Lambert law. In this method we systematically analysed to find best absorption transition pair for sensitive measurement of temperature in the target combustion environment using a single tunable diode laser. The ratio of absorption of two transitions is only function of temperature, so from ratio of absorption of two transition lines, we will get temperature. Ones we know the temperature then we can calculate species concentration from absorption of any one transition line using Beer-Lambert law.

Water vapor is present in ambient air as well as a primary hydrocarbon combustion product, and thus an important target for absorption-based sensors. There are nearly half a million-possible water vapor absorption transitions catalogued between 1 and 2 μm, and a crucial element in the design of a tunable-diode-laser absorption-based sensor is the selection of optimum transitions. All the fundamental spectroscopic parameters like line strength, line centre frequency, lower state energy etc. are available at databases and we can simulate line shape to a pair of water lines, which is appropriate in our experimental conditions.

A.2 Theory of absorption spectroscopy

A.2.1 Beer-Lambert law

The theoritical principle of absorption spectroscopy is based on Beer-Lambert law. The equation of Beer-Lambert law is:

$$T_\nu \equiv (I/I_0)_\nu = exp(k_\nu.L) \tag{A.1}$$

where T_ν is the fractional transmission; I and I_0 are the transmitted and incident laser intensities; k_ν (cm^{-1}) is the spectral absorption coefficient; L (cm) is the path length.

The spectral absorption coefficient k_ν (cm^{-1}) comprising N_j overlapping transitions in a multi-component environment of K species can be expressed as[1]

$$k_\nu = P\sum_{j=1}^{K} X_j \sum_{j=1}^{N_j} S_{i,j}(T)\mathit{\Phi}_{i,j}(\nu - \nu_{0,i}) \tag{A.2}$$

where P [atm] is the total pressure, X_j is the mole fraction of species j, $S_{i,j}$ ($cm^{-2}atm^{-1}$) and $\mathit{\Phi}_{i,j}$ (cm) are the linestrength and lineshape of a particular transition i of the species j, respectively. S(T) is fundamental spectroscopic property and depends on only temperature. $\mathit{\Phi}(\nu - \nu_{i,0})$ describe the effect of collisional and thermal processes and depends on temperature, pressure, gas composition, and mechanisms of line broadening.

The area underneath lineshape function $\mathit{\Phi}_{i,j}$ is normalized to unity so that

$$\int_\nu \mathit{\Phi}_{i,j}(\nu - \nu_{i,0})d\nu \equiv 1 \tag{A.3}$$

A.2.2 Lineshape function

There are teo kind of broadening mechanisms; homogeneous broadening and inhomogeneous broadening. Homogeneous broadening (e.g. natural lifetime broadening and collisional broadening) which affects all molecules in the same way whereas inhomogeneous broadening (e.g. Doppler broadening) which has different effects on different groups of molecules. Beacuse of different broadening mechanisms, a specific absorption transition may be a convolution of multiple lineshape functions. The lineshape function provides important information since it is a function of many parameters such as pressure, species concentration and temperature. There are many lineshape functions available to describe the broadening mechanisms and those are Gaussian, Lorentzian, Voigt, Hartmann–Tran profile (HTP) etc. The IUPAC recommended Hartmann–Tran profile (HTP) as the standard profile[4].

A.2.3 Temperature Measurement

The two-line technique is usufull method for temperature measurement in scanned wavelength spectroscopy[1]. The gas temperature is obtained by comparing the line strength of two different transitions which have different temperature dependence[5]. The temperature-dependent linestrength ($cm^{-2}atm^{-1}$) can be expressed as follows:

$$S(T) = S(T_0)\frac{Q(T_0)}{Q(T)}(\frac{T_0}{T})exp[-\frac{hcE"}{k}(\frac{1}{T}-\frac{1}{T_0})][1-exp(\frac{-hc\nu_0}{kT})][1-exp(\frac{-hc\nu_0}{kT_0})]^{-1} \tag{A.4}$$

where Q(T) is the molecular partition function, h (J sec) is Planck's constant, c (cm/s) is the speed of light, k (J/K) is Boltzmann's constant, and E" (cm^{-1}) is the lower-state energy.T_0 is the reference temperature.

The temperature can be calculated from the measured ratio of integrated absorbance for two different temperature-dependent transitions which is simply the ratio of line strengths (as two integrated absorbances are obtained with the same partial pressure of water and same path length).

$$R = \frac{A_1}{A_2} = \frac{\int P_{abs}L\Phi_{\nu_1}S_1(T)d\nu}{\int P_{abs}L\Phi_{\nu_1}S_1(T)d\nu} = \frac{S_1(T)}{S_2(T)} = \frac{S(T_0,\nu_1)}{S(T_0,\nu_2)}exp[-(\frac{hc}{k})(E_1"-E_2")(\frac{1}{T}-\frac{1}{T_0})] \tag{A.5}$$

where P_{abs} (atm) is the partial pressure of the absorbing species, Φ_ν (cm) is the line-shape function of a particular transition, $S(T_0, \nu_i)$ is the line strength of the transition centered at ν_i (cm^{-1}), for the reference temperature T_0; E" is the lower state energy (cm^{-1}), and T is the gas temperature (K).

Temperature,

$$T = \frac{\frac{hc}{k}(E_2" - E_1")}{\ln\frac{A_1}{A_2} + \ln\frac{S_2(T_0)}{S_1(T_0)} + \frac{hc}{k}\frac{(E_2" - E_1")}{T_0}} \tag{A.6}$$

A.2.4 Species Concentration Measurement

The integrated absorbance is proportional to partial pressure. So, species concentration,

$$X = \frac{A}{\int PL\Phi_\nu S(T)d\nu} = \frac{A}{PLS(T)} \tag{A.7}$$

where P (atm) is the total pressure, L (cm) is the path length, S(T) (cm^{-2}/atm) is the line strength and A (cm^{-1}) is the integrated area.

A.3 Spectroscopic database

An important step in the water absorption sensor design is the line selection. HITRAN[6] and HITEMP[7] are high-resolution transmission molecular absorption database. We used the HITRAN Application Programming Interface (HAPI)[8] to simulate the transmission and emission line of water.

A.4 Line Selection

Figure A.2 shows all the water transitions. Among these lines, we select two line based on the following criteria:

1. Both lines need sufficient absorption over the selected temperature range.

Minimum detectable absorption be greater than 10^{-3} and peak absorption preferably be less than 0.05.

2. Transition should be relatively free of ambient H_2O interference.

This difficulty can be removed by choosing transition with high lower state energy (E" $\geq 1700cm^{-1}$).

3. The absorption lines must lie within a single laser scan and not overlap significantly at atmosphere pressure.

Spectral separation of the line pairs must lie between 0.3 and 1 cm^{-1}.

4. The two lines should have sufficiently different lower state energies E" to yield a ratio that is sensitive to the probed temperature.

$$\mid \Delta E"_i \mid = \mid E"_1 - E"_2 \mid \geq 700cm^{-1}$$

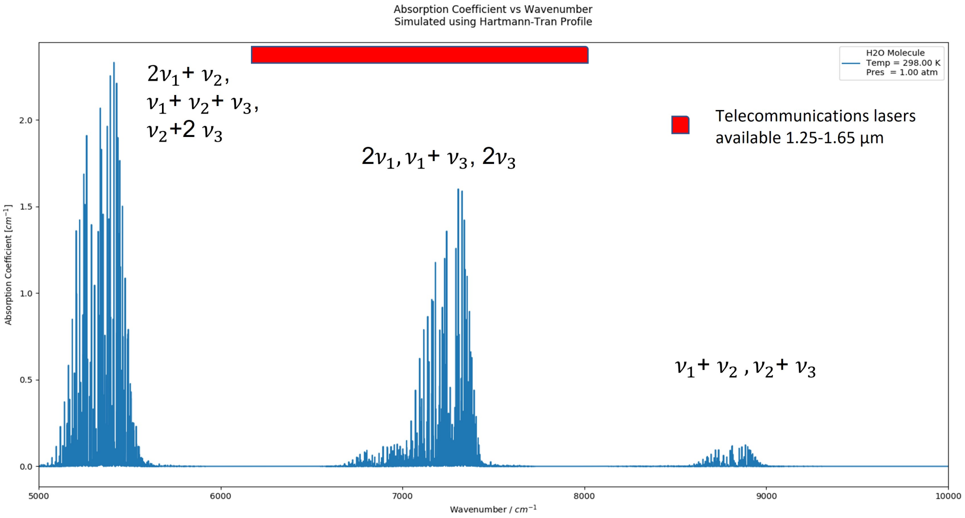

Figure A.1: A simulated water spectrum using Hartmann-Tran Porfile. Data taken from HITRAN-2016 data base.

5. The two should be free of significant interference from nearby transitions.
6. The wavelength should be in the 1.25-1.65 μm range.

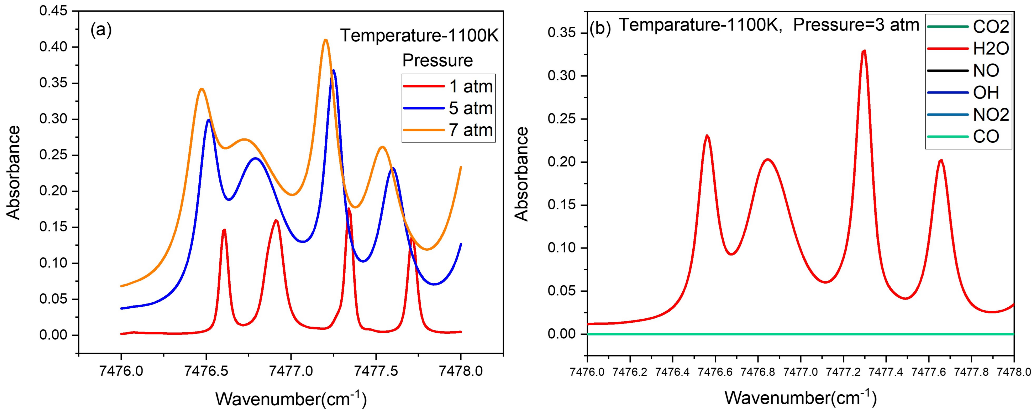

Figure A.2: (a) Absopbance of water at 1100K and 1,5, and 7 atm. (b) Absorbance of H_2O, CO_2, NO, OH, NO_2, and CO at 1100K and 3 atm. Data taken from HITRAN-2016 data base.

Based on these criteria we have selected line pair ($7476.94cm^{-1}\&7477.36cm^{-1}$) for our experiment. Figure A.2 (a) shows the absopbance of those water line pair at 1100K and 1,5, and 7 atm. Figure A.2 (b) shows absorbance of H_2O, CO_2, NO, OH, NO_2, and CO.

A.5 Experimental setup

Figure A.3 shows the schemetic diagram of experimental setup.

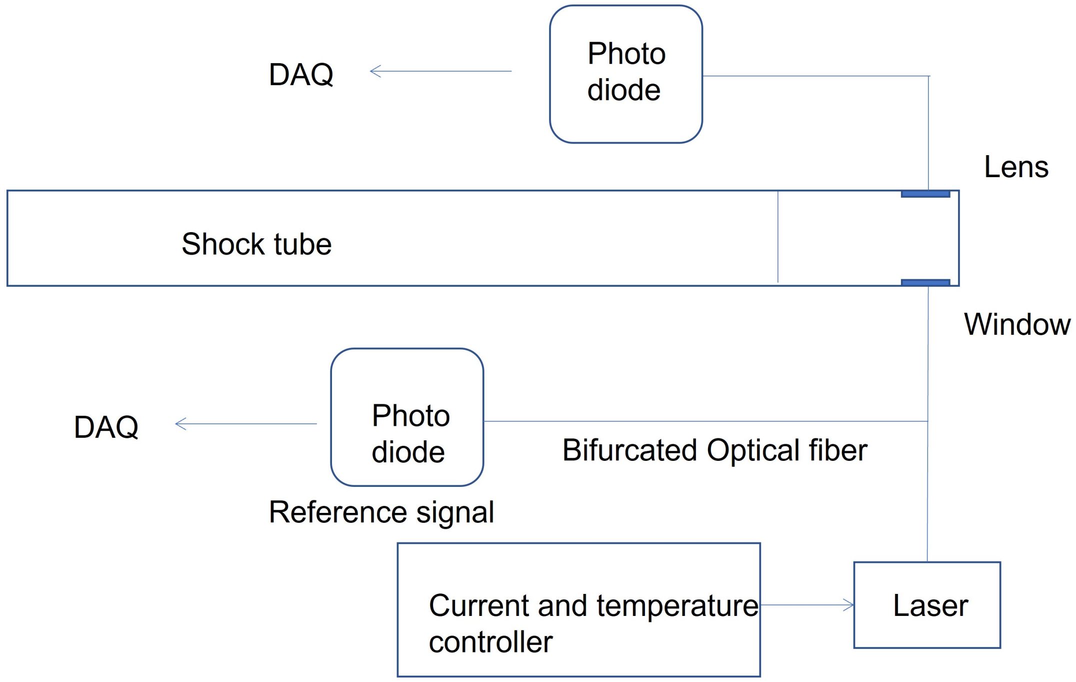

Figure A.3: Schematic diagram of Scanned-wavelength direct absorption spectroscopy.

Diode laser is connected with current and temperature controller to scan the desire wavelength. Using optical fibre and windows, we connect laser with one side of shock-tube. We used photo diode as a detector. Photo diode is connected with opposide side of shock tube using optical fibre and lens. Finally photo diode connected with DAQ for data acquisition.

A.6 Equipment

1. Laser: Laser Diode 1337.7 nm,DX-1 module, eblanephotonics. Inbuild current and temperature controller.

2. Photodiode: Model 818-BB-31, High Speed Photodetector, 1000-1600 nm Battery Biased InGaAs Detector, 1.5 GHz, Newport.

3. Window: Sapphire Window, 6.35 mm Diameter, 0.50 mm Thick, Model SAW12, Newport.

4. Lens: Plano-Convex Lens, N-BK7,6.35 mm Diameter, 6.4 mm EFL, Uncoated, Model KPX010, Newport.

A.7 Conclusion

Using a single diode laser we can accurately measure temperature and concentration of water molecule in a combustion environment. Based on six criteria we have selected line pair (7476.94 cm^{-1} & 7477.36 cm^{-1}) for our experiment. We brought all the equipment based on our design. It is hoped that these results will be useful in future development of this technique.

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