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Gas Phase Reactions of Cyclopentadiene with CH and OH Radicals

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Gas Phase Reactions of Cyclopentadiene with CH and OH Radicals

Kacee L. Caster

Dissertation Submitted
to the Eberly College of Arts and Sciences
at West Virginia University

in partial fulfillment of the requirements for the degree of
Doctor of Philosophy in Chemistry/Physical Chemistry

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2021

Keywords: Gas Phase Reactions, Small Free Radicals, Photoionization Mass Spectrometry, Rate Constant, Pulsed Laser Photolysis, Laser-Induced Fluorescence, First Ring, Benzene, Cycloaddition, Fulvene, Resonantly Stabilized Radicals

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Abstract

Gas Phase Reactions of Cyclopentadiene with CH and OH Radicals

Kacee L. Caster

The formation of polycyclic aromatic hydrocarbons (PAHs) and carbon-based nanoparticles in combustion environments is driven by the pyrolysis and oxidation of abundant fuel molecules. The subsequent growth of these pyrolytic byproducts is then propagated by reactions with small free radical species like OH, CH, O atoms, and C₂H. Cyclopentadiene (C₅H₆) is a significant five-member combustion intermediate that has been detected in many high temperature reactions, such as in the pyrolysis of jet fuels like JP-10. Experimental and theoretical investigations in the reactions of cyclopentadiene with these small free radical species are necessary towards understanding the initial rate-limiting steps in the overall PAH growth scheme. Experimental kinetic rate constants are obtained for the CH(X²Π) radical reaction with cyclopentadiene under pseudo-first order conditions in a quasi-static reaction cell. The CH(X²Π) radical is generated by pulsed laser photolysis (PLP) of bromoform (CHBr₃) at 266 nm and the concentration is monitored using laser-induced fluorescence (LIF) at an excitation wavelength of 430 nm. Isomeric products and associated branching ratios are measured for CH and OH radical reactions with cyclopentadiene using multiplexed photoionization time-of-flight mass spectrometry coupled to synchrotron radiation at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratories in Berkeley, California. Density functional theory and CBS methods are used to calculate the potential energy surface for mechanistic discussions of the previous reactions. Master Equation calculations using the MESMER open-source program are performed to infer product branching ratios about the respective products. Evidence supports a fast, barrierless cycloaddition of the CH radical along the pi-bonds of the five-member ring to form C₆H₆ isomers (benzene, fulvene, among others) and a H atom. Preliminary results from the OH radical reactions suggest the main pathway follows association to form C₅H₆OH isomer intermediate thoroughly a weakly bonded van der Waal's complex. This intermediate can be stabilized at higher pressures or undergo H atom loss to form the final products, C₅H₅OH.

To my grandmother, *Patricia Ann O'Neil Wilson* –

whose love and support gave me a start in life,
and whose memory gives me strength to carry on.

This is for you.

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List of Symbols and Abbreviations

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2-C ₅ H ₅ OH	Cyclopenta-1,3-dien-1-ol
2-C ₅ H ₆ OH	Cyclopentenyl-2-ol
3-C ₅ H ₅ OH	Cyclopenta-1,3-dien-2-ol
3-C ₅ H ₆ OH	Cyclopentenyl-3-ol
1245HT	1,2,4,5-hexatetraene
12HD5Y	Hexa-1,2-dien-5-yne
13HD5Y	Hexa-1,3-dien-5-yne
1E13BD	Trans-/Cis-1-ethynyl-1,3-butadiene
2E13BD	Cis-2-ethynyl-1,3-butadiene
34DMCB	3,4-dimethylenecyclobutene
1D	One Dimensional
2D	Two Dimensional
3D	Three Dimensional
ALS	Advanced Light Source
B3LYP	Becke, 3-parameter, Lee-Yang-Parr

CBS	Composite Basis Set
CHRCR	Clustering of Hydrocarbons by Radical-Chain Reactions
cm ³	Cubic Centimeters
CPD	Cyclopentadiene
CPDyl	Cyclopentadienyl
DFT	Density Functional Theory
DG	Delay Generator
eV	Electronvolt
FWHM	Full Width Half Maximum
FTIR	Fourier Transform Infrared Spectroscopy
HACA	Hydrogen-Abstraction-C ₂ H ₂ -Addition
HAMA	Hydrogen-Abstraction-Methyl-Addition
HAVA	Hydrogen-Abstraction-Vinylacetylene-Addition
Hz	Hertz
IDP	Interplanetary Dust Particles
ILT	Inverse LaPlace Transform
INT	Intermediate
IR	Infrared Spectroscopy
IRC	Intrinsic Reaction Coordinate
ISM	Interstellar Medium

K	Kelvin
kJ	Kilojoules
KrF	Krypton Fluoride
L	Liter
LIF	Laser-Induced Fluorescence
M	Molarity
MCP	Microchannel Plate
ME	Master Equation
MESMER	Master Equation Solver for Multi Energy Well Reactions
MFC	Mass Flow Controller
mJ	Millijoules
MPIMS	Multiplexed Photoionization Mass Spectrometry
ms	Milliseconds
Nd:YAG	Neodymium Yttrium Aluminum Garnet
nm	Nanometer
NMR	Nuclear Magnetic Resonance
NO _x	Nitrogen Oxides
ns	Nanoseconds
Pa	Pascals
PAH	Polycyclic Aromatic Hydrocarbon
PES	Potential Energy Surface
PIMS	Photoionization Mass Spectrometry

PLP	Pulsed Laser Photolysis
ppm	Parts per Million
PMT	Photomultiplier Tube
RBF	Round Bottom Flask
RRKM	Rice-Ramsperger-Kassel-Marcus
RSRs	Resonantly Stabilized Radicals
s	seconds
sccm	Standard Cubic Meters per Minute
slm	Standard Liters per Minute
SO _x	Sulfur Oxides
TOF-MS	Time-of-Flight Mass Spectrometry
TMC-1	Taurus Molecular Cloud-1
TS	Transition State
TST	Transition State Theory
μs	Microseconds
UV	Ultraviolet
VDW	van der Waals
VOCs	Volatile Organic Compounds
VUV	Vacuum Ultraviolet
ZPE	Zero Point Energy

Chapter 1: Introduction

1.1 Carbon Rich Environments

Chemical reactions in the gas phase can lead to very complex chemical mechanisms and are still not well understood. Understanding the fundamental reactions occurring in gas phase environments could provide insight into the larger molecular growth schemes that form carbon-based particulates. Examples of carbon-based particulates range from soot, a byproducts of the combustion of fuels, or grain structures on asteroids and interplanetary dust particles (IDP), as shown in Figure 1.1¹, that may contain the necessary elements (C, H, O, N, P, and S) for the basis of life as we know it. Such molecular growth schemes are complicated by the presence of abundant species and are not yet well-defined.

Figure 1.1 Secondary electron image of an interplanetary dust particle (IDP) obtained using transmission electron microscopy. Image Credit: Bradley et al., *Science*, 2005.¹

The universe is endless and vast, and filled with many diverse carbon-rich gas phase environments waiting to be studied. From planetary atmospheres like those of Saturn's moon Titan to gas giants like Jupiter, to chemically rich molecular clouds like TMC-1 that provide the primordial ingredients for star formation and areas of the interstellar medium that are the basis of the universe we know, molecular growth begins in the gas phase. On asteroids, such as the recently discovered and explored 162173 Ryugu (Figure 1.2²), the mechanistic study of the formation of

ice grain structures begins in the gas phase. Here on Earth, we are not only concerned with the same atmospheric processes as these extraterrestrial planetary environments, but also the impact that carbon particulates like soot, which results from man-made and naturally occurring combustion processes, have on our environment and health. The predictive capability of models that focus on replicating the complexity of these carbon-rich environments is still very limited by a lack of relevant kinetic and thermodynamic in these carbon-based molecular growth schemes.

Figure 1.2 Monochrome image of the asteroid 162173 Ryugu, as it appeared at 20 km from the Japan Aerospace Exploration Agency (JAXA) spacecraft, Hayabusa2. Image Credit: JAXA, University of Tokyo and collaborators.²

1.1.1 Combustion Environments

In combustion processes, a high-temperature, exothermic chemical reaction occurs between a fuel source and some type of oxidant. These reactions usually produce a great deal of useable energy in the form of heat or work. Ideally, these processes would occur completely to produce energy and a limited range of coproducts, such as CO_2 and H_2O . However, most combustion processes are incomplete as oxygen is a limiting reagent in most relevant environments and the fuel source does not completely react. When incomplete combustion occurs, various other reactants and byproducts in addition to CO_2 and H_2O are produced, such as: CO , carbon-based particulate matter, volatile organic compounds (VOCs), and unburned fuel sources (hydrocarbons), among others. In the case of nitrogen-containing fuel sources, nitrogen oxides

(NO_x) and other nitrogen-containing byproducts can also be produced.^{18–21} In addition to the creation of unwanted and harmful byproducts, incomplete combustion reactions release less energy than desired and are overall inefficient and wasteful.

Most of the Earth's energy sources are obtained from the burning of fossil fuels which undergo incomplete combustion. The modern combustion engine, powered by gasolines from fossil fuel sources, is a prime example of inefficient combustion. Typical engines that power our vehicles only have ~12–30% fuel efficiency, depending on the features and drive cycle of the vehicle.²² These factors serve as a large motivator in understanding the chemical reactions occurring in combustion processes so to increase the efficiency and energy produced. In addition, a great deal of human interest lies in the study of combustion byproducts and their formation. Most of these emissions are known carcinogens and pollutants and have adverse health and environmental effects for much of the world's population. Nitrogen oxides (NO_x) and sulfur oxides (SO_x) are common byproducts that contribute to smog, acid rain, increasing ozone concentrations, and adverse health effects.^{23,24} Carbon monoxide (CO) is another known contributor to pollution, such as smog, and is poisonous and fatal to humans in appreciable quantities. Many hydrocarbon species byproducts are known carcinogens, including unsaturated (1,3-butadiene, etc.), saturated alkanes, monoaromatics (benzene, styrene, etc.) and polycyclic aromatic hydrocarbons (PAHs; pyrene, naphthalene, etc.). These hydrocarbons are known to further react in a much larger chemical growth scheme to form carbon particulate matter, like soot; however, this scheme is still not well understood. To reduce these emissions and the adverse effects they have, the mechanism of formation must be better understood.

1.1.2 Extraterrestrial Environments and Planetary Atmospheres

The chemistry of molecules of the universe, whether it occurs between stars, around stars or in planetary atmospheres, is a complex yet rapidly evolving field. Due to the difficulties of study such long-range reactions, there is a need to understand the fundamental reactions in these unique extraterrestrial environments. These extraterrestrial molecules begin in supernovae, the highly explosive death of stars which emit gas and dust that provide the basis for the formation of new galaxies. Over time, these supernova emissions coalesce with the aid of gravity to form the components of the interstellar medium (ISM): diffuse clouds, protoplanetary nebulae, and circumstellar envelopes, etc. In the interstellar medium, the area comprising the matter and radiation between galaxies, is rich with ionic, atomic, and molecular species in the gas phase; approximately 99% of the ISM is believed to be composed of these gaseous species.²⁵ While most of the ISM is composed of hydrogen and helium, atomic carbon is the fourth most abundant element in the universe. Carbon atom and carbon-containing molecular reactions could lead to the formation of PAHs in these environments.

PAHs are believed to make up to ~20% of the carbon-containing molecules in the universe.^{16,26,27} There is also evidence to suggest their presence and role in the evolution of the interstellar medium.^{28–33} Once formed, PAHs can aggregate to ultimately form much larger nanoparticle structures, such as carbonaceous interstellar dust particles or ice grain structures. The understanding of extraterrestrial chemistry and interstellar environments is still limited by an understanding of how first ring and ultimately larger structures, such as prebiotic molecules, leading are formed in the gas phase.³⁴

1.2 Polycyclic Aromatic Hydrocarbons

When abundant fuel molecules react in air (O_2/N_2) through incomplete combustion, many reactive intermediate species are formed. These intermediate species, such as small free radicals, hydrocarbon species, resonantly stabilized radicals (RSRs) and atoms, are known to further react and participate in a larger molecular growth schemes leading to carbon nanoparticles, such as soot. Polycyclic aromatic hydrocarbons (PAHs) are known to be molecular precursors to these carbon nanoparticles in carbon-rich environments, such as combustion flames,^{3,35} planetary atmospheres,³⁶ and the interstellar medium^{28,37–39} and are an integral part of the molecular growth scheme. In combustion processes, PAHs aggregate to form soot, which is a known carcinogen and pollutant.^{3,35,40} Their formation is initiated during the pyrolysis and oxidation of fuel or hydrocarbon molecules and proceed through reactions with free radicals such as OH, O atom, C_2H , and CH, as shown in Figure 1.3.^{3,28,41,42} These radicals propagate growth in the molecular zone of the growth scheme in Figure 1.3, leading to the first aromatic ring (e.g., benzene, styrene, etc.) and eventually to peri-condensed aromatic rings (e.g., naphthalene, anthracene, pyrene, etc.), which ultimately aggregate to form soot.

Figure 1.3 Schematic depicting the formation of soot in premixed flames. Image Credit: H. Richter and J.B. Howard, *Progress in Energy and Combustion Science*, 2000.³

PAHs are widely abundant in combustion processes and there is also evidence to suggest their presence and role in the evolution of the interstellar medium.^{28–33} Commonly accepted PAH growth schemes center on repetitive reactions and include the well-known HACA (Hydrogen-Abstraction- C_2H_2 -Addition)^{17,20,21}, HAMA (Hydrogen-Abstraction-Methyl-Addition),⁴³ or CHRCR (Clustering of Hydrocarbons by Radical-Chain Reactions)⁴⁰, among others. In general, these mechanisms proceed by sequential hydrogen abstraction from an aromatic molecule followed by addition of an intermediate to the subsequent radical site. Similar mechanisms replacing acetylene/methyl with propargyl and cyclopentadienyl radicals also lead to the formation of large PAHs.^{11–15} The significance of the various pathways is largely dependent on the structure of the fuel molecule and the reaction conditions.⁴⁹ In addition, the formation of the first ring is

generally regarded as the main rate-limiting step in the overall molecular growth scheme and has been widely studied.^{35,42,50}

1.2.1 HACA Mechanism

The widely accepted HACA mechanism can lead to the formation of larger PAHs in carbon-rich environments and has been extensively studied through experiment and theory over the years.^{41,51–55} The repetitive mechanism proceeds through two steps: (a) abstraction of a hydrogen atom from an aromatic ring followed by (b) addition of an acetylene (C_2H_2) molecule. This repetitive process is compelled by the H atom abstraction in environments where H atoms are abundant and reactive and can repeat to form peri-condensed aromatic rings. The mechanism is generally believed to begin with monoaromatic rings, such as benzene, but is also capable of initiating from small PAH byproducts. Scheme 1.1 shows an example of the HACA mechanism beginning from benzene (C_6H_6).

Scheme 1.1 HACA mechanism example beginning from benzene leading to the formation of naphthalene.

Molecular hydrogen can abstract an H atom from the benzene ring to form the phenyl radical (C_6H_5) and H_2 . In the next step, acetylene (C_2H_2) adds to the radical site of the phenyl molecule and form phenylacetylene (C_8H_7). If the process repeats a second time, H abstraction

from the ring of phenylacetylene can form a radical which ultimately forms naphthalene through acetylene addition. The hydrogen abstraction and resulting radical site of the reacting molecule will ultimately determine the structure of the PAH formed. Additionally, other small free radical species, such as the OH radical, can initiate the HACA mechanism.

1.2.2 Other Repetitive PAH Growth Mechanisms

Variations of the HACA mechanism have been proposed and studied over the years^{40,43,53,56} and typically involve other hydrocarbon and radical species abstracting and/or adding to the radical site of a hydrocarbon. The HAMA (Hydrogen-Abstraction-Methyl-Addition)⁴³ mechanism was studied experimental using photoionization mass spectrometry techniques and is suggested to be involved in the formation of first aromatic rings including styrene, toluene, and xylene. Once these first rings are formed, molecular growth can proceed through subsequent repetitive reactions.

Another repetitive PAH growth mechanism that was recently proposed is the HAVA ((Hydrogen-Abstraction-Vinylacetylene-Addition) mechanism, first experimentally determined through crossed molecular beam reaction studies of the phenyl radical (C_6H_5) with vinylacetylene ($HCCC_2H_3$) leading to the formation of naphthalene ($C_{10}H_8$).⁵⁶⁻⁵⁸ Scheme 1.2 shows this reaction mechanism.¹⁶

Scheme 1.2 HAVA mechanism example proceeding through the addition of vinylacetylene to the radical site of the phenyl radical and leading to the formation of naphthalene.¹⁶

Vinylacetylene first adds to the radical site of the phenyl radical through a barrierless process to form a weak van der Waals complex. This weak complex can then isomerize to a resonantly stabilized radical, which can further isomerize through hydrogen migration and ring closure steps to form a naphthalenyl radical. The two-ring radical can then undergo H atom elimination to form naphthalene. Because of the initial formation of the van der Waals complex and the lower energy (submerged) barriers, the HAVA mechanism could potentially lead to the formation of PAHs in low-temperature, interstellar environments. Unlike the HACA mechanism, the HAVA mechanism can lead to the formation of larger PAH structures containing more than 3 rings.

1.3 Small Free Radicals

The importance of small free radical species like the CH radical in the formation of PAHs in carbon-rich environments has been long established.^{3,40,42,48,59} Small free radical species, such as hydroxyl (OH), methyldene (CH), cyano (CN), are abundant in combustion and extraterrestrial environments. They are integral in propagating molecular growth in these environments through

reactions with other hydrocarbon molecules or radical species. In addition, resonantly stabilized radicals (RSRs), such as propargyl (C_3H_3), allyl (C_3H_5), and phenyl (C_6H_5), are known to accumulate in appreciable quantities in combustion environments. These RSRs are defined by one or more unpaired electrons that can distribute over multiple sites of the molecule thus creating resonance structures, as shown in Figure 1.4. RSRs are typically less reactive with stable oxidizing molecules (O_2), in comparison to other radical species. The self- or cross- recombination of RSRs is an evolving area in the study of PAH formation.

Figure 1.4 Examples of resonance structures of commonly discussed resonantly stabilized radical species.

1.3.1 CH Radical Reaction Mechanism

The highly reactive methyldidyne radical (CH) plays a significant role in carbon-rich environments and its reaction with a series of relevant hydrocarbon species has been extensively studied.^{5–7,60–62} It was one of the first radicals detected in the interstellar medium,⁶³ it is also believed to play a role in planetary atmospheres where methane abundance is significant, such as in Saturn's moon, Titan.⁶⁴ The CH radical can also form during the pyrolysis of hydrocarbon fuels

and other combustion processes and is mostly removed through reactions with abundant fuel molecules.^{65–67}

One of the most reactive small free radical species in combustion environments is the methylidyne (CH) radical. This radical is unique in structure due to a singly occupied and a vacant non-bonding molecular orbital centralized on the carbon atom, in addition to a filled orbital that also lends a carbene-like nature.⁶⁸ The reaction mechanisms of the CH radical with unsaturated hydrocarbons involve little to no barrier, leading to reactions proceeding at a fraction of the collision rate. The initial encounter of the reactants is followed immediately by the formation of an initial, short-lived intermediate that isomerizes and decomposes to give the final products. These initial short-lived intermediates are typically formed through either CH insertion into a C–H σ -bond or through cycloaddition across the C=C π -system of the reacting molecule. CH radical reactions can be summarized in a general chemical scheme described by a CH-addition-H-elimination mechanism: $\text{CH} + \text{C}_n\text{H}_m \rightarrow \text{C}_{n+1}\text{H}_m + \text{H}$.⁶⁹ General CH radical mechanisms suggest that the reaction is more likely to proceed through a singlet-carbene-like cycloaddition across the π -system of the molecule to form a three-membered ring constituent, as shown in Scheme 1.3.⁶⁸ This initial intermediate may rapidly ring open or isomerize, and further dissociate through hydrogen elimination to form the final products. In the absence of π -bonds, as in the case of the CH reaction with CH_4 ,^{60,70–72} the measured rate coefficients still remains fast indicative of a barrierless CH insertion into the sigma C–H bonds of the molecule (Scheme 1.3). Recent investigations into the products of the CH + pyrrole ($\text{C}_4\text{H}_5\text{N}$) reaction from Soorkia et al.⁷³ strongly support the cycloaddition pathway as the dominate channel. The authors propose a 4-step ring expansion pathway following the general CH mechanism that results in the formation of six-

membered pyridine (C_5H_5N) + H. Ultimately the favorability of the entrance channel mechanism is based upon the nature of the initial reactant.^{68,69}

Scheme 1.3 CH radical reaction mechanisms in the example of the reaction with cyclopentadiene (C_5H_6).

The reaction rate of CH radicals with unsaturated hydrocarbons have been extensively studied over the past few decades.^{5,6,60,69,71,74–77} Canosa et al.⁶⁰ studied the experimental rate coefficients for CH reactions with ethylene (C_2H_4) and butene (C_4H_8) over a temperature range of 23 to 295 K using pulsed-laser photolysis (PLP) and laser-induced fluorescence (LIF) to probe the radical decay. At 295 K, rate coefficients of $k_{C_2H_4} = 2.92 (\pm 0.22) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{C_4H_8} = 3.70 (\pm 0.25) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ were reported. Fast and pressure-independent rate coefficients were observed down to 23 K. The rate coefficients displayed a slight positive temperature dependence from 23 K up to 75 K, where a maximum was reached, after which a negative temperature dependence dominated up to 295K. This negative temperature dependence is consistent with a rapid, barrierless CH addition mechanism, as proposed by Butler et al.⁷ in their study of $CH + C_2H_4$. Canosa and coworkers⁶⁰ also suggested that the kinetics below room temperature was governed by long-range electrostatic forces between the reactants.

Berman et al.⁵ measured rate coefficients using pump-probe laser techniques at room temperature for the reactions with ethylene ($k_{C_2H_4} = 4.2 (\pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), benzene ($k_{C_6H_6} = 4.3 (\pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), and toluene ($k_{C_6H_5CH_3} = 5.0 (\pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). In the case of ethylene, the rate coefficients displayed a negative temperature dependence over a temperature range of 160 to 652 K. For the CH + benzene reaction, the rate coefficient was found to be independent of temperature over the 297 to 674 K range,⁵ although the authors were unable to conclude with certainty on this result due to systematic error from photodissociation of benzene in the reaction cell. Goulay et al.⁷⁸ studied the reaction of CH with anthracene ($C_{14}H_{10}$) and reported similar collision-limit rate coefficients with a slight positive temperature dependence over the 58–470 K temperature range.

The reaction of the CH radical with conjugated cyclic molecules is believed to favor cycloaddition onto the unsaturation to form a ringed intermediate. In the case of the reactions with methyl substituted furan molecules,^{79,80} this intermediate isomerizes through ring opening to form mostly non-cyclic final products. For reaction with pyrrole (C_4H_5N), Soorkia et al.⁷³ identified the six-membered ring, pyridine (C_5H_5N), as the sole contributing isomer to the product channel, supporting the ring expansion mechanism through CH cycloaddition.

1.3.2 OH Radical Reaction Mechanism

The reaction rate and mechanism of the OH radical with hydrocarbons has been studied extensively through experiment and theory over the years.^{81–90} The OH radical can form during the pyrolysis of fuel molecules and further react with hydrocarbon species to produce oxygenated species in combustion and atmospheric processes. The OH radical plays a significant role in the oxidative degradation of tropospheric species, most notably benzene.⁹¹ The resulting products from these reactions are typically carcinogenic and toxic. Consumption of aromatic products in

the combustion of fuels is largely initiated through oxidative reactions with species like the OH radical. Thus, there is a general need to understand the mechanism behind OH radical reactions over a range of conditions.

The OH radical is capable of three main reaction mechanisms, as shown in Scheme 1.4: abstraction, association, and addition. In OH abstraction mechanisms, the OH radical abstracts a hydrogen from the reactant to produce H_2O and a radical species which can participate in further reactive schemes. In the example of OH radical reaction with CPD, the abstraction produces the resonantly stabilized cyclopentadienyl radical (C_5H_5) + H_2O . The OH radical can also undergo association with an unsaturated hydrocarbon to form a pre-reactive van der Waal's complex. This van der Waals complex can stabilize into an intermediate adduct and undergo further isomerization or elimination reactions. In higher pressure conditions, this stabilization of the adduct increases the overall reaction rate and the intermediate could be detectable, depending on the resolution and sensitivity of the instruments used in experiment. Finally, the OH radical can add to unsaturated $\text{C}=\text{C}$ bonds of reactants to form an oxygenated species. As shown in Scheme 1.4, the OH radical reacts with the $\text{C}=\text{C}$ bond of CPD to form an intermediate species, which can undergo hydrogen atom elimination to form cyclopentadienol.

Scheme 1.4 OH radical reaction mechanisms in the example of the reaction with cyclopentadiene (C_5H_6).

1.4 The Role of Benzene

The formation of benzene (C_6H_6) in carbon-rich gas phase environments, such as those involving planetary atmospheres,^{36,92} the interstellar medium (ISM),^{28,57,93,94} and combustion processes,^{3,41,95} has long been of interest in many theoretical and experimental studies. Owing to its overall high stability and resistance to oxidation, benzene is regarded as one of the key intermediates and its formation is believed to be a rate-limiting step in larger carbon molecule growth schemes leading to the formation of PAHs and ultimately carbon nanoparticles.^{96–98}

Figure 1.5 Structures of small free radical species that lead to the formation of benzene and their corresponding references.

Benzene formation is typically modeled through the reactions of resonantly stabilized radicals, such as propargyl (C₃H₃), allyl (C₃H₅), butynyl (*i*-C₄H₅), and cyclopentadienyl (C₅H₅), as shown in Figure 1.5.^{9,99-101} The self-recombination of the propargyl radical in a head-to-tail (head: H₂C•- and tail: =C•H) fashion is the most familiar route to benzene formation, as well as several other linear C₆H₆ isomers, and has been extensively studied through theory and experiment.^{96,102-105} Experimental studies in 1,3-butadiene (H₂CCHCHCH₂) flames indicate that the *i*-C₄H₅ + C₂H₂ reaction may also compete with propargyl recombination for benzene formation.¹⁰⁶ To a lesser extent, benzene may also be formed by the cross-recombination of the propargyl and allyl radicals.^{99,107} However, the dominant benzene formation mechanism is likely to depend on the relative concentration of the propargyl radical and therefore on the chemical composition of the environments.^{59,108} In addition, for reactions involving self- or cross-recombination of resonantly stabilized radicals, the final product distribution will be very sensitive to the temperature and pressure of the environment.¹⁰⁹ In the interstellar medium, at low temperatures and number densities, stabilization of the initially-formed reaction adduct is very improbable, and benzene is

more likely to be formed by addition of carbon-centered radicals with a closed shell molecule. Jones et al.⁹³ proposed the C_2H + butadiene ($H_2CCHCHCH_2$) as a possible benzene source at low temperatures based on analyses of molecular scattering data obtained in crossed-molecular beam experiments. These results remain to be reconciled with the direct detection of mainly fulvene (*c*- $C_5H_4=H_2$) + H, following the 248-nm photolysis of a C_2HBr + butadiene mixture at room temperature and 4 Torr under multiple collision conditions using photoionization mass spectrometry (PIMS) techniques, performed by Lockyear et al. to investigate the reaction between C_2H and butadiene.¹³ A better understanding of benzene formation in carbon-rich environments requires a systematic investigation of all possible benzene-forming reactions involving a range of open and closed shell intermediates.

1.5 Cyclopentadiene in Combustion

Cyclopentadiene (CPD, C_5H_6) is an abundant conjugated combustion intermediate that has been shown to play a central role during the formation of aromatic molecules^{11,110–112} It has been detected during the pyrolysis of toluene ($C_6H_5CH_3$) and benzyl radical ($C_6H_5CH_2$).^{113,114} The oxidation of benzene has also been shown to produce significant amounts of cyclopentadiene over the 300–1000 K temperature range.¹¹⁵ More recently, CPD has been identified as a major product during the pyrolysis of the jet fuel JP-10 with branching fractions greater than 15% reported over the 1300–1600 K temperature range.¹¹⁶ These product fractions are in good agreement with prior experimental studies conducted over a wide range of temperatures and pressures suggesting CPD as a major product.^{110,117–120} Vandewiele et al.¹¹⁰ examined the secondary reaction products of JP-10 pyrolysis and found that CPD was the central first ring involved in the formation of PAHs such as naphthalene and indene. Theoretical models also suggest that the addition of the cyclopentadienyl radical to the neutral CPD molecule provides additional routes to naphthalene

and indene.¹²¹ Further reaction of the formed PAHs with CPD could yield fluorenes, which are larger three and four ring PAH structures with five-membered ring constituents.¹¹² The presence of five-membered rings in PAHs has been shown to facilitate isomerization and dimerization in these molecules and to effectively contribute to higher sooting tendencies during combustion processes.^{122,123} Although CPD is an important combustion intermediate during PAH formation, its reactions with reactive combustion intermediates has largely been overlooked.

1.6 Relevance of Research

Based upon the mechanistic evidence discussed in the previous sections and its rapid reactions with unsaturated molecules, the CH radical is likely to be capable of facilitating molecular growth and possibly ring expansion in cyclic unsaturated hydrocarbons in gas phase environments. Its reaction with unsaturated cyclic molecules, such as CPD, could play a major role during the PAH-growth rate-limiting first ring formation step. Based upon the CH + pyrrole mechanism of Soorkia et al.¹⁷, the reaction of the CH radical with cyclopentadiene could follow a similar ring expansion mechanism and lead to the formation of benzene. The identification of cyclopentadiene in the pyrolysis of several conventional fuels has been the subject of recent publication^{124–128} while the abundance of the CH radical in combustion has been long established. The rate constants of the CH radical with unsaturated hydrocarbons have been determined to be fast, near the collision limit, and barrierless. If both of these reacting species were present in appreciable quantities, the reaction of CH radical with cyclopentadiene could prove to be a viable and competitive route to the formation of an important first-ring species, benzene, as shown in Scheme 1.5. The accurate measurement of the rate coefficients and product detection for such reactions contributes to improving the accuracy of molecular growth models.

Scheme 1.5 Proposed mechanism for the CH radical reaction with cyclopentadiene based upon the mechanistic study from Soorkia et al.¹⁷

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Chapter 2: Experimental and Computational Methods

2.1 Kinetic Experiments

Kinetic investigations on the $\text{CH}(\text{X}^2\Pi)$ radical reaction with CPD (C_5H_6) were performed in a quasi-static reaction cell over pressure ranges of 2.7–9.7 Torr and temperature ranges of 298–450 K. The reaction was studied in the quasi-static reaction cell using a two-laser pump-probe technique and under pseudo-first order kinetic conditions to determine the overall second order rate constant for the reaction.

2.1.1 Quasi-Static Reaction Cell

The kinetic measurements are performed in a six-way-cross stainless steel, quasi-static reaction cell. Figure 2.1 shows a schematic of the reaction cell used in the experiment. The four horizontal ports allow for laser access between the pump-probe lasers with the lasers intersecting in the center region of the reaction cell. Each port entrance contains a 1" uncoated UV-fused silica window at the Brewster angle (53°) to minimize the reflection of the vertically-polarized laser beam. Connections to $\frac{1}{4}$ " copper tubing are available on the four horizontal ports for injection of the gaseous species. A 100 Torr capacitance manometer (Baratron, MKS Instruments) is connected to one of the horizontal ports to monitor the pressure inside the reaction cell. Vacuum in the reaction cell is maintained through connection to a vacuum pump on one of the horizontal ports while the pressure inside the reaction is regulated from approximately 2 to 10 Torr using a manual butterfly valve. A small amount of N_2 buffer gas ($\sim 3\%$ of the total flow) is introduced adjacent to the length of the pump laser port to avoid deposition of the radical precursor. The lower vertical port is closed off using a stainless-steel flange. The upper vertical port contains a quartz window

for UV light transmission and supports the photomultiplier tube (PMT), which collects the UV light from the experiment. A plano-concave lens is inserted into the inner portion of the upper vertical port to collect the laser-induced fluorescence signal. The PMT contains a 490 nm (10 nm FWHM) filter to collect the CH LIF signal.

Figure 2.1 Schematic of the quasi-static reaction cell used for kinetics measurements of the CH radical with cyclopentadiene.

The temperature in the reaction cell is controlled using heating tape wrapped on the outside of the reaction cell that is regulated through a feedback loop. A retractable Type K thermocouple is placed close to the center region of laser-overlap in the reaction chamber to monitor and regulate the gas temperature.

2.1.2 Gas Introduction

Argon is used as the main buffer gas, making up the majority of the total gas flow. Liquid bromoform (CHBr_3 , Sigma-Aldrich, 99%) is used as the CH radical precursor and is kept in a glass bubbler maintained at a constant temperature of $\sim 8^\circ\text{C}$ using a temperature-controlled water bath. Argon gas is used as the carrier gas to bubble through the radical precursor and introduce a small fraction (~ 5 to 10%) into the overall gas flow. The pressure inside the bubbler is controlled through valves and monitored using a 1000 Torr capacitance manometer (Baratron, MKS Instruments). Cyclopentadiene (CPD) reagent is prepared through the thermal cracking of dicyclopentadiene ($\text{C}_{10}\text{H}_{12}$), where the distillate is collected in a liquid nitrogen trap and then vacuum transferred into a 3.79 L stainless steel cylinder. A detailed description of the cyclopentadiene synthesis has been given previously and is described in more detail in the Appendix.^{129,130}

All of the gaseous species (argon, nitrogen, cyclopentadiene reactant in nitrogen, and bromoform precursor) are introduced into the flow using calibrated mass flow controllers (MKS instruments) and connected to the experiment through $\frac{1}{4}$ " copper tubing. The gases are premixed and preheated in a 50 cm^3 stainless steel mixture chamber before introduction into the reaction cell. The flow rates for all the gaseous species are corrected for calibration of the mass flow controllers.

2.1.2.1. Calibration of Mass Flow Controllers

To correctly determine the flow rates and number densities of the gaseous species used in the experiment, the mass flow controllers must be calibrated. Custom-made cylinders of a known volume are used to calibrate the mass flow controllers (MFCs). For MFCs with higher flow rates (1–5 slm), a cylinder of volume = 8.549 L is used, while MFCs with lower flow rates (20–200

sccm) use a smaller cylinder of volume = 1.023 L. The cylinders are connected to the MFCs, and a capacitance manometer is attached to the setup to monitor and record the pressure inside the cylinder as a function of time. The setup is tested for leaks in the lines and the cylinders are initially evacuated to a pressure below 0.1 Torr. Variable amounts of argon buffer gas then flown into the setup through the mass flow controllers and the pressure in the cylinders as a function of time is recorded. The recorded pressures over the set time are then plotted and fit to a linear equation to determine the standard flow rate (q_v^0) per the equation below:

$$q_v^0 = \dot{P} \frac{V}{P^0} \frac{T^0}{T} \quad (1)$$

where V is the measured volume of the cylinder and copper tube lines; P^0 is standard pressure (101,325 Pa); T^0 is standard temperature (273.15 K); and T is the temperature of the calibration gas (room temperature, 298 K). By fitting the pressure versus time readings, a value for the slope, $\dot{P}$, is determined as shown in Figure 2.2.

Figure 2.2 Plot of the recorded change of pressure versus time used to determine the standard (actual) flow rate in calibration of a 20 sccm mass flow controller.

Once a value for the standard flow rate (q_v^0) is determined from the equation, a plot of the measured flow rates versus the set flow rates (from the MFC) is created, as shown in Figure 2.3.

Fitting the points to a line reveal a slope and y-intercept value that can be used to determine the actual flow rate:

$$Q_{act}^0 = m \times Q_{read}^0 - b \quad (2)$$

where Q_{act}^0 is the actual flow rate adjusted for MFC calibration, m is the slope from the plot, Q_{read}^0 is the flow rate recorded from the MFC, and b is the y-intercept from the plot.

Figure 2.3 Plot of actual flow rate versus the set flow rate for determination of the correction factor for a 100 sccm mass flow controller.

2.1.3 Pulsed Laser Photolysis/Laser-Induced Fluorescence

Pulsed Laser Photolysis/Laser-Induced Fluorescence (PLP/LIF) is a spectroscopic technique that is commonly referred to as a pump-probe technique.¹³¹ In pump-probe spectroscopy, one laser, usually of a stronger beam, is used to generate the reacting species of interest in an excited state (pump laser), while the second laser is used to excite and detect the species of interest (probe laser). The change in LIF signal as a function of delay time between the pump-probe laser yields information about the excited state of the species of interest, in this case the concentration or reaction rate of a radical reactant. The PLP-LIF technique gained popularity in the 1980's, with a renewed interest in reaction kinetics of gas phase molecules and is still used

today. It is an extensively used technique that has been incorporated into many kinetic studies of gas-phase reactions involving radicals in combustion environments, planetary atmospheres, and the interstellar medium.^{5–7,60,130,132–138}

In PLP, a high-power laser in the UV or visible region is used to create the radical of interest by breaking the bonds of a precursor. The laser pulse width is shorter than the lifetime of the radical of interest. The second portion of the technique, LIF, involves the excitation of the generated radical species from a lower rovibronic state to a higher rovibronic state through absorption of a photon. The wavelength of absorption typically corresponds to a maximum wavelength of absorption for the electronic transition of the radical as shown in Figure 2.4. Once the radical is excited, it will relax spontaneously back to a lower vibronic state and emit radiation, which can then be collected using a detector such as a photomultiplier tube (PMT) or photodiode.

Figure 2.4 CH LIF spectrum for $A^2\Pi \leftarrow X^2\Sigma$ electronic transition ($v'=0, v''=0$).

2.1.3.1 Generation and Detection of the CH Radical

In this work, a fixed wavelength Nd:YAG laser at 266 nm is the pump laser for the Pulsed Laser Photolysis (PLP), while a tunable dye laser pumped by a second Nd:YAG laser at 355 nm is the probe laser used in Laser-Induced Fluorescence (LIF). In PLP, a laser beam creates the

radical reactant by breaking the bonds of a precursor material. In the reaction of CH radicals with CPD, bromoform (CHBr_3) serves as the CH radical precursor and is generated through a successive two photon absorption of the fourth harmonic of the Nd:YAG laser at 266 nm:

Absorption of the first photon by bromoform results in excited state CHBr^* and bromide as shown in R1, while the second photon is introduced in the same laser pulse to break the bonds of the CHBr^* intermediate and create the ground state $\text{CH}(\text{X}^2\Pi)$ radical and molecular bromine.^{62,139}

Often times, however, an unwanted third photon is introduced in this succession to create the first excited state $\text{CH}(\text{A}^2\Delta)$ radical:¹⁴⁰

The first electronic excited state of the $\text{CH}(\text{A}^2\Delta)$ radical is easily identifiable in experiments by a strong emission immediately after photolysis of the precursor ($t=0$), with a very short lifetime of $\sim 3 \mu\text{s}$ such that it does not typically interfere with experiments as shown in Figure 2.5. A small flow of nitrogen ($< 5\%$ of the total flow) is introduced alongside the bromoform flow to quench the vibrationally excited $\text{CH}(\text{X}^2\Pi, v=1)$ state formed during the photolysis of the precursor also shown in Figure 2.5.¹³⁸

Figure 2.5 LIF Signal of the CH radical collected at 430.8 nm showing the decay of the radical as a function of delay time between the lasers. The lifetimes of the excited electronic and vibrational states are noted as well as the time where the exponential decay is measured (30–100 μs).

The CH($X^2\Pi$) radicals are then excited on the $A^2\Delta$ ($v=0$) $\leftarrow$ $X^2\Pi$ ($v=0$) vibronic band at 430 nm using a 355 nm pumped dye laser with Stilbene 420 dye (Exciton). The LIF signal of the CH radical from the $A^2\Delta$ ($v=0$) $\rightarrow$ $X^2\Pi$ ($v=1$) vibronic band at 480 nm is collected by the PMT through a 490 nm (FWHM ± 10 nm) band-pass filter. The collected fluorescence is integrated over a 1.1 μs gate, 500 ns after the probe laser pulse and averaged using an SRS 250 Boxcar Integrator. Relative radical number density temporal profiles are obtained by changing the delay time between the pump/probe lasers using a delay generator (SRS DG535) with 1 μs delay steps and averaging 10 laser shots per point. The temporal profiles are fit using an exponential decay from 30 μs to 100 μs after the pump laser pulse as shown in Figure 2.5. Earlier times are not included in the fit to avoid any effect from the N_2 -collisional relaxation of the CH ($X^2\Pi$, $v=1$) radicals.¹³⁸

2.1.4 Principles of Pseudo-First Order Kinetics

The CH radical reaction with cyclopentadiene is a bimolecular reaction (second order reaction). To study the bimolecular reaction and minimize the associated complexities of measuring the concentrations of both reactant species, a pseudo-first order approximation is applied to the kinetic study. A pseudo-first approach involves introduction of one of the reactant species in large excess relative to the other such that it can be neglected. For the reaction of CH radical with cyclopentadiene, the CPD reactant is introduced in excess relative to the concentration of the CH radical.

Under pseudo-first order conditions, the CH LIF decay signal due to its reaction with cyclopentadiene is given by the following equations:

$$[CH]_t = [CH]_0 e^{-k_{1st}\Delta t} \quad (3)$$

$$k_{1st} = k_{2nd}[C_5H_6] + k'_{1st} \quad (4)$$

where k_{2nd} is the overall second-order rate constant of the CH ($v=0$) + cyclopentadiene reaction; Δt is the delay time between the photolysis and probe lasers; $[CH]_0$ and $[CH]_t$ refer to the initial CH radical concentrations in the cell and at a delay time (Δt); $[C_5H_6]$ is the number density of the cyclopentadiene reactant introduced; k_{1st} is the pseudo first-order rate constant for the CH radical decay; and k'_{1st} is the first-order rate constant for loss of CH by reaction with its precursor ($CHBr_3$) and other possible photoproducts such as $CHBr$, Br_2 , Br and CBr . For a constant bromoform flow rate, the concentrations of the precursor photolysis products remain constant within a given dataset. The experiments are repeated for various concentrations of cyclopentadiene to obtain the second order rate coefficient at a given pressure and temperature under pseudo-first order conditions. The temporal profiles of the CH LIF signal are fit using an exponential function to determine a value for k_{1st} using Eq. (3).

Figure 2.6 Temporal profiles of the CH LIF decay as a function of cyclopentadiene concentration. The CH decays increase with increasing [CPD] and are fit to an exponential from 30–100 μs delay time (red, green, and blue lines).

The integrated CH LIF signal is plotted against laser delay time for various cyclopentadiene number densities as shown in Figure 2.6. The k_{1st} values obtained from the exponential fits and Eq. (3) are then plotted against the cyclopentadiene number density to extract the overall second-order rate constant for the reaction as shown in Eq. (4). Figure 2.7 shows a typical k_{2nd} plot recorded at 298 K and 5.3 Torr. The good linearity of the fit supports the pseudo first-order approximation. The slope of the fit in Figure 2.7 is used to determine the second-order rate coefficient.

Figure 2.7 Typical plot of k_{1st} versus the number density of cyclopentadiene recorded at 298 K and 5.3 Torr. The k_{2nd} value is obtained using a linear fit to the data per Eq. (4) and reported with 2 σ uncertainty.

2.1.6 Validation of the Reaction Cell

The setup was validated before the experiment through determination of the second-order rate coefficient of the previously studied CH radical reaction with ethylene (C₂H₄). The weighted k_{2nd} value for the CH radical reaction with ethylene was measured to be $2.57 (\pm 0.14) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, which is in good agreement with previous measurements as shown in Figure 2.8.⁴⁻⁷ Validation of the high temperature setup over the 298 to 450 K range has been achieved from previous experiments.^{82,89}

Figure 2.8 Comparison of the experimentally determined k_{2nd} value (open circles, with 2σ uncertainty) from this work for the reaction of $\text{CH}(\text{X}^2\Pi)$ radical with ethylene with previous studies.⁴⁻⁷

2.2 Product Detection Experiments

Although many techniques have been developed to study the chemical kinetics of gas phase reactions over the years, much difficulty remained with the identification of the isomeric reaction products and their underlying mechanisms. The Multiplexed Photoionization Mass Spectrometry (MPIMS) apparatus at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratories in Berkeley, CA, was developed to provide a solution to these difficulties in studying chemical reactions in the gas phase. The MPIMS apparatus was developed and reported by Osborn et al⁸ in *Review of Scientific Instruments* in 2008, and has been used extensively over the years to provide deeper insight into gas phase chemical reactions and isomeric resolution of the involved

neutral reactants, intermediates, and products. In this work, the MPIMS apparatus was used in the product detection studies of OH and CH radicals with CPD.

2.2.1 Multiplexed Photoionization Mass Spectrometry (MPIMS) Apparatus

A schematic adapted from the instrumental review by Osborn et al.⁸ is shown in Figure 2.9. The apparatus consists of four main parts: the flow tube and vacuum source, the photoionization source, the mass spectrometer, and the ion detector/data acquisition system. The chemical reaction begins in a 62 cm slow-flow quartz tube with a 1.05 cm inner diameter. Reactant, buffer, and precursor gases are injected into the reactor tube through calibrated mass flow controllers. The flow velocity is set at $\sim 5 \text{ m s}^{-1}$ to replenish the gas mixture between each laser pulse. A pulsed, unfocused KrF excimer laser propagates along the length of the tube at 4 or 10 Hz to initiate the reaction and generate the radical of interest. The KrF excimer laser is capable of wavelengths of 193, 248, and 351 nm with a fluence range of 10–60 mJ cm^{-2} . The pressure in the flow tube is measured using a capacitance manometer and connected to a Roots pump that is controlled through a feedback loop and evacuates the flow tube. The temperature in the flow tube is wrapped in nichrome tape and regulated through a thermocouple 3 cm downward from the point of extraction. The flow tube is capable of temperatures over the 300–1050 K range. Experimental conditions in the flow tube for this study are typically held at 4 Torr and 298 or 373 K with a total gas flow rate of 100 sccm, such that the total number density is approximately $1 \times 10^{17} \text{ cm}^{-3}$. The reaction tube was heated to 373 K in the CH + CPD reaction after several runs to avoid deposition of the radical precursor. A 650-micron diameter pinhole, approximately halfway down the length of the tube, allows for extraction of the irradiated gas mixture.

Figure 2.9 Schematic of the multiplexed photoionization mass spectrometer at the Advanced Light Source used in the product detection experiments and reprinted from Osborn et al.⁸

The extracted irradiated gas mixture is transferred into a vacuum chamber and passed through a 0.15 cm diameter skimmer to generate a molecular beam. The molecular beam enters the ionization region where VUV quasi-continuous synchrotron radiation can then form ions in the gas mixture. The formed ions are then detected using a 50 kHz orthogonal-acceleration time-of-flight mass spectrometer (TOF-MS) culminating in a time- and position-sensitive microchannel plate (MCP) detector for data collection. The TOF-MS operates in relation to the KrF excimer laser pulse to monitor the species of interest. The resulting time-resolved mass spectra are normalized for variations in the VUV photon flux, which is continuously monitored via a

photodiode placed after the ionization point. The apparatus allows for 3-dimensional data sets that reveal information about the kinetic time, the ionization energy, and the mass of the species of interest. The combination of the various data sets allows for isomeric resolution in the product detection.

2.2.1.1 Advantages Relative to Other Techniques

The MPIMS apparatus was developed with several capabilities in mind: universal, selectivity, sensitivity, and detection (multiplexed). A universal MPIMS allows for the study of all atoms and molecules using tunable VUV synchrotron radiation from the Chemical Dynamics Beamline 9.0.2 of the Advanced Light Source Synchrotron at Lawrence Berkeley National Laboratories. The synchrotron at the ALS is capable of radiation over the 7.2–25 eV range with a brightness of 10^{21} photons cm^{-2} sr^{-1} and a resolution of $E/\Delta E \sim 1000$.⁸ The brightness of the synchrotron radiation allows for higher sensitivity while the tunability provides a higher selectivity. The use of a multiplexed mass spectrometer allows for more efficient detection of multiple species simultaneously.

2.2.1.2 Gas Introduction

Bromoform and cyclopentadiene (C_5H_6) are introduced in small amounts relative to the helium buffer gas, which composes most of the total flow rate. A small fraction (15%) of nitrogen is added to sufficiently quench any vibrationally excited CH resulting from the photolysis of the bromoform precursor.¹³⁸ Liquid bromoform is held in a glass bubbler at a temperature of approximately 10.0 °C and pressure of 600 Torr and its vapor is carried into the main carrier gas flow by a controlled amount of helium flow. Cyclopentadiene (CPD) reagent is prepared through the thermal cracking of dicyclopentadiene ($\text{C}_{10}\text{H}_{12}$), where the distillate is collected in a liquid nitrogen trap and then vacuum transferred into a 3.79 L stainless steel cylinder. A detailed

description of the cyclopentadiene synthesis has been reported previously^{129,130} and is described in more detail in the Appendix. Helium buffer gas filled the remaining volume of the cylinder so that the total pressure was approximately 2023 Torr and the final mixture contained 4.67% CPD. The resulting CPD number density in the reaction flow tube was approximately 4.8×10^{13} molecules cm^{-3} .

Under the experimental conditions, collisional quenching with the He and N₂ buffer gases is expected to rapidly thermalize all the products to the temperature of the flow. As long as the unimolecular dissociation of the reaction intermediates occurs with a rate higher than the collision rate ($<20 \times 10^6 \text{ s}^{-1}$), the present branching ratios provide information about the unimolecular isomerization and dissociation scheme of the nascent reaction intermediates.

2.2.1.3 Collection of Data in 3D

Photoion spectra are recorded by averaging at least 500 laser shots at each energy step over a kinetic time range of 0–80 ms at 4 Hz or 10 Hz, relative to the laser pulse. The setup allows for collection of data sets in three dimensions: cation intensity vs. mass-to-charge ratio (m/z), kinetic time (t), and photon energy (E). The data are baseline subtracted for pre-photolysis signals using the 20 ms time range before each laser pulse and normalized for the VUV photon energies. Plotting the data in two-dimensional data sets provides mass spectra that are resolved for either photon energy or kinetic time. Positive ion signals in the mass spectra indicate species created during and after the laser pulse, whereas negative ion signals indicate the species that are depleted due to the laser pulse. Photoionization spectra are obtained by taking a 1-D slice over the mass species of interest from the 2-D energy-resolved mass spectra. The photoionization spectra enable identification of different isomers appearing at a single mass of interest through decomposition of each observed spectrum into the spectra of its individual isomeric components. When experimental

photoionization spectra of pure isomers exist, they are utilized as basis functions. For an isomer without an experimental spectrum, the photoionization spectrum is predicted from the integral of calculated Franck-Condon factors, assuming that direct ionization dominates. A linear least-squares fit of a set of basis functions to the experimental spectra observed in the CH + C₅H₆ reaction enables quantification of each isomer if the absolute photoionization cross sections are known. The photoionization spectra are reported as individual measurements with error bars reported from the shot noise in the number of the detected ion counts ($\sqrt{N}$).

2.3 Theoretical Calculations

To better understand the connection between the experimentally determined rate constants and branching ratios obtained from the product detection experiments, theoretical calculations are incorporated into this work. The potential energy surface (PES) of the CH and OH radical reactions with cyclopentadiene are examined. Master Equation calculations using the open-source MESMER software are conducted on the CH radical reaction with cyclopentadiene to further investigate the reaction mechanism.

2.3.1 Calculations on a Potential Energy Surface

The CH(X²Π) + C₅H₆(X¹A₁) and OH(X²Π) + C₅H₆(X¹A₁) potential energy surfaces (PES) are calculated using the Gaussian 09 suite of programs.¹⁴¹ Geometry optimizations and frequency calculations of all stationary points on the PES are first performed using hybrid DFT methods at the B3LYP/CBSB7 level.¹⁴² Analysis of the resulting vibrational frequencies ensures that all stationary points are characterized as local minima or first-order saddle points. Single-point energy calculations are performed using the composite CBS-QB3 method to obtain more accurate energy values for all stationary points.^{143–145} The transition states are located by scanning the changes in geometry (bond lengths, bond angles, etc.) between intermediates using B3LYP/6-31G(d) and

confirmed as first-order saddle points by the presence of an imaginary frequency. After single-point energy calculations on the transition state using the CBS–QB3 method, intrinsic reaction coordinate (IRC) calculations are then performed using B3LYP/6-31G(d) to verify the connectivity of the optimized transition state structures to the corresponding minima along the reaction coordinates. The described method was used to locate transition states for the entrance channels of the reaction; however, none were found.

2.3.2 Master Equation

2.3.2.1 Principles of MESMER

Figure 2.10 Schematic of the processes involved in the MESMER calculations.

The modelling of gas phase reactions over an extended range of temperature and pressures provides a certain validation to the experiment. In chemical kinetics, the Master Equation is used to describe the probabilistic states of a chemical system as a function of time. Figure 2.10 shows a schematic of the processes on the PES involved in the ME calculations by MESMER. However, finding a solution to the Master Equation has proved difficult without the use of theoretical

calculations. Over the years, various programs have been developed to provide a solution to the Master Equation. The MESMER software uses matrix techniques to provide a solution to the ME of a unimolecular system consisting of any number of energy wells, transition states, sinks, and reactants (Figure 2.10).¹⁴⁶ In this study, the open-source master equation solver MESMER (Master Equation Solver for Multi Energy well Reactions) is applied to the study of the PES for the CH radical reaction with cyclopentadiene.

2.3.2.2 Master Equation Calculations

Branching fractions for the products of the $\text{CH}(\text{X}^2\Pi) + \text{cyclopentadiene}$ reaction are calculated using the open-source master equation solver MESMER (Master Equation Solver for Multi Energy well Reactions). Given stationary points of the potential energy surface (PES), MESMER solves coupled differential equations describing the reaction and energy transfer kinetics. The methodology has been described in detail by Glowacki et al.¹⁴⁶ and has been employed to investigate OH radical reactions with unsaturated hydrocarbons as well as the CH radical reaction with ammonia.^{147,148}

The heats of formation for stationary points on the PES for the CH + CPD system, were previously calculated using density functional theory (DFT) and CBS-QB3 methods.¹³⁰ Unimolecular rates for isomerization and decomposition of the reaction intermediates are calculated using the RRKM theory. RRKM theory is a microcanonical transition state theory connecting traditional transition state theory (TST) with statistical theories.¹⁴⁹ RRKM theory uses given energies from *ab initio* calculations to calculate the microcanonical rate constant, $k(E)$. In the case of barrierless processes, such as the entrance channel and the bicyclic + H dissociation channel, the rates are calculated with a normal and reverse inverse Laplace transform (ITL). For

the H-loss channels, the kinetic parameters used for the model are those for the addition of an H atom onto benzene. Energy transfer processes between intermediates and the buffer gas are modeled using a constant average energy transfer in the downward direction, ΔE_{down} (Table 2.1).

The classical rotor approximation is used for all intermediates as suggested by Pakhira et al.¹⁵⁰ for molecules with rotational constants well below 1 cm^{-1} . Tunneling effects are not investigated since the goal is only to obtain a general trend for the evolution of the branching ratios at high temperatures. The energy grain size typically used for the modeling is 50 cm^{-1} , while a larger grain size of 100 cm^{-1} is used for the sensitivity analysis. The energy transfer and Lennard-Jones parameters are taken from previous work on CH and OH reactions with unsaturated hydrocarbon and are displayed in Table 2.1.^{148,150} The number density of cyclopentadiene in the ME calculations ranges from $1\text{--}10 \times 10^{13}\text{ cm}^{-3}$.

Table 2.1 Master Equation parameters and their associated scanning range significant to the MESMER calculations.

	$\Delta E_{down}\text{ (cm}^{-1}\text{)}$	$\varepsilon\text{ (cm}^{-1}\text{)}$	$\sigma\text{ (\AA)}$
Intermediates	250 (100 – 800)	380 (300 – 600)	4.3 (2 – 6)
Products	250 (100 – 800)		
Argon		11.4	3.47
Nitrogen (N ₂)		48	3.9

2.4 References

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Chapter 3: Reaction of the CH(X²Π) Radical with Cyclopentadiene

3.1 Kinetic Measurements

Table 3.1 Experimental conditions and reported overall CH + CPD rate coefficients for independent data sets. Reported error is 2σ obtained from the linear fit of the k_{2nd} plots.

T (K)	η _{total} (10 ¹⁷ molecules cm ⁻³)	[CPD] Range (10 ¹² molecules cm ⁻³)	Laser Fluence (mJ cm ⁻²)	k _{2nd} (10 ⁻¹⁰ cm ³ s ⁻¹)
298	1.73	27.8–116.1	104	3.81 ± 0.25
298	1.72	23.6–98.6	111	2.97 ± 0.15
298	1.74	23.9–99.9	110	2.82 ± 0.36
298	1.74	23.9–99.9	111	2.31 ± 0.20
298	1.72	23.5–98.4	108	2.46 ± 0.20
298	1.72	23.9–99.8	111	2.52 ± 0.18
298	1.72	24.1–100.7	110	3.69 ± 0.27
298	1.73	23.6–98.5	92	2.88 ± 0.23
298	1.72	27.3–114.2	92	3.37 ± 0.14
298	1.71	27.1–113.4	88	3.61 ± 0.18
298	1.74	24.1–100.9	99	2.43 ± 0.24
298	1.74	24.1–100.9	94	1.68 ± 0.15
298	3.13	50.3–210.3	104	2.85 ± 0.32
298	0.90	12.5–52.1	108	3.17 ± 0.38
350	1.49	20.3–84.7	92	3.42 ± 0.26
350	1.51	20.5–85.8	92	2.83 ± 0.30
350	1.55	24.6–102.7	88	2.54 ± 0.27
400	1.32	18.0–75.2	92	1.99 ± 0.21
400	1.35	18.3–76.6	92	3.10 ± 0.21
400	1.41	17.6–74.4	88	2.57 ± 0.15
450	1.29	20.6–86.0	92	1.98 ± 0.89
450	1.31	16.5–69.3	88	2.19 ± 0.14

The weighted average k_{2nd} value for all data sets collected for the CH radical reaction with cyclopentadiene at 5.3 Torr and 298 K was measured to be $2.7 (\pm 1.3) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Table 3.1 displays the experimental conditions and measured rate coefficients for all the CH + cyclopentadiene reaction data collected over a range of conditions.

3.1.1 Statistical Analysis

The experimentally determined k_{2nd} values were reported to 2σ error bars. The data sets were analyzed within a 95% confidence level using a weighted statistical analysis. A weighted analysis takes into consideration the number of individual measurements (k_{1st} values) and the associated uncertainties with that specific measurement and weights them accordingly in the overall average k_{2nd} value.¹⁵¹ The average k_{2nd} value ($\bar{x}_W$) is determined through Equation 1:

$$\bar{x}_W = \frac{\sum w_i x_i}{\sum w_i} \quad (1)$$

where x_i is individual measurement (k_{1st} value) and w_i is the weighted uncertainty from an individual measurement (k_{1st}), which is calculated from the measured uncertainty (σ_i) as shown in Equation 2:

$$w_i = \frac{1}{\sigma_i^2} \quad (2)$$

The final weighted rate constant values ($\bar{x}_W$) are reported with a weighted uncertainty (σ_w) calculated using Equation 3:

$$\sigma_w = \frac{1}{\sqrt{\sum w_i}} \quad (3)$$

Finally, Chauvenet's criteria is used to test for any data sets that are suspected of being outliers. The basic principles of the test are to calculate a probability band that based on the mean of a normal distribution containing all the data sets. If the suspected data set is outside of this probability band, then it can be considered an outlier and removed. Chauvenet's criteria states that

“if the expected number of measurements at least as deviant as the suspect measurement is $< \frac{1}{2}$, then reject the suspect measurement”¹⁵¹ and is calculated using Equation 4:

$$t_{sus} = \frac{x_{sus} - \bar{x}_w}{\sigma_w} \quad (4)$$

where t_{sus} is the standardized deviation from the mean for all suspect values, x_{sus} is the measurement suspected of being an outlier, $\bar{x}_w$ is the weighted average determined from Equation 1, and σ_w is the weighted uncertainty determined from Equation 3. The value for t_{sus} is then compared to values from a table of 95% level confidence intervals to determine its viability in the overall calculations.

3.1.2 Fluence Dependence

The absorption cross section for cyclopentadiene has been measured to be $4.8 \times 10^{-19} \text{ cm}^2$ at 266 nm,¹⁵² and its dissociation at 248 nm is known to produce various reactive products, including the cyclopentadienyl (C_5H_5) and propargyl (C_3H_3) radicals. The photodissociation process may decrease the number density of reactants in the flow (within 5.5% to 7.0% of the initial reactant number density) and the photoproducts may react with the CH radical and interfere with the kinetic measurements. To investigate the effect of 266 nm photolysis on the reaction rate coefficient, k_{2nd} values were measured as a function of laser fluence (total energy per unit surface). Figure 3.1 displays the measured rate coefficients as a function of laser fluence within the 88–112 mJ cm^{-2} range. The values for the laser fluence associated with the data set can be found in Table 3.1. The reaction rate coefficient displays no identifiable laser-fluence dependence within the investigated fluence range. Any dependence on the laser fluence is within two standard deviation of the overall rate coefficient and does not significantly affect the results.

Figure 3.1 Second-order rate coefficient (k_{2nd}) as a function of laser fluence at 298 K. Each individual data point is presented with error bars reported to 2σ uncertainty.

3.1.3 Pressure Dependence

The pressure dependence of the overall CH + cyclopentadiene rate coefficient is studied over the 2.7–9.7 Torr range. Figure 3.2 shows the second order rate coefficients reported with vertical error bars representing 2σ error over the specified pressure range. The standard deviation is obtained by weighting the k_{1st} values by the 2σ error obtained from the individual linear fits versus cyclopentadiene number density plots. The k_{2nd} values for each corresponding point are averaged from at least three independent data sets obtained from different cyclopentadiene samples. The individual rate constants over the specified range of pressure are in good agreement within 2σ error of each other. This suggests that the second order rate constant is pressure independent over the specified experimental range.

Figure 3.2 Second-order rate coefficient (k_{2nd}) as a function of total cell pressure at 298 K. Each data point is the average of multiple runs with error bars reported to 2σ precision (see Table 3.1).

3.1.4 Temperature Dependence

Validation of the high temperature setup over the 298 to 450 K range has been achieved from previous experiments.^{82,89} The temperature dependence of the overall rate constant of the CH + cyclopentadiene reaction is studied over the 298–450 K range. Figure 3.3 shows the second order rate constants reported with vertical error bars representing 2σ error up to 400 K. The corresponding k_{2nd} values are obtained in the same manner as previously described, except for the data point at 450 K. Only two independent data sets were obtained at 450 K due to difficulties arising from optimization of the CH LIF signal at higher temperatures. For the 450 K data, the unweighted average is recorded and the uncertainty in the average is reported from the corresponding minimum and maximum values of the two data sets. The individual rate constants over the specified range of temperature are in good agreement within 2σ error of each other,

suggesting no observable temperature dependence over the specified experimental temperature range.

Figure 3.3 Second-order rate coefficient as a function of the cell temperature at 5.6 Torr. Each data point is a weighted average from at least 3 independent datasets with error bars reported to 2σ precision. The 450 K point (filled circle) is the average of two data sets reported with the minimum and maximum values.

3.2 Potential Energy Surface Calculations

Since no information about the identity of the products from the reaction can be determined from the kinetic experiments, a portion of the C_6H_7 potential energy surface was computed to better understand the reaction mechanism. The reaction mechanisms of the CH radical with unsaturated hydrocarbons involve little to no barrier, leading to reactions proceeding at a fraction of the collision rate. The initial encounter of the reactants is followed immediately by the formation of an initial, short-lived intermediate that isomerizes and decomposes to give the final products. These initial short-lived intermediates are typically formed through either CH insertion into a C-H σ -bond or through cycloaddition across the C=C π -system of the reacting molecule. CH radical

reactions can be summarized in a general chemical scheme described by a CH-addition-H-elimination mechanism: $\text{CH} + \text{C}_n\text{H}_m \rightarrow \text{C}_{n+1}\text{H}_m + \text{H}$.⁶⁹

In this work, the CH cycloaddition and insertion mechanisms using DFT and CBS-QB3 are calculated to complement the experimental results. All the energy values provided are relative to the reactants: cyclopentadiene and the CH radical. Figure 3.4 shows the C_{2v} symmetry in the structure where the sp^3 hybridized carbon is labeled C1 and the remaining sp^2 carbons are described as C2 and C3, respectively. The PES is split into two separate pathways by way of entrance channel mechanism. The enthalpies for the products of the hydrogen abstraction pathways as well as several acyclic products are computed and examined further in the Discussion Section but not included in the displayed PES.

Figure 3.4 Representation of the CH radical reaction sites of the carbons of cyclopentadiene for the purpose of discussion of the potential energy surface entrance channels.

A comparison of the energetics from previous C_6H_7 PES theoretical calculations^{15,153,154} to the present calculations using CBS-QB3 methods can be found in Tables 3.2 and 3.3. Calculated values for the PES are in good agreement with the previous studies; any discrepancies in the values are due to the differences in the method and level of theory used for the calculation.

Table 3.2 Comparison of the stationary points for the C₆H₇ PES involving H-assisted isomerization of fulvene to benzene. All values are relative to fulvene + H and reported in units of kJ/mol. Empty cells refer to stationary points not located in that reference.

Stationary Points	Label (PES)	Jasper et al. ¹⁵³ (M06-2X/6-311++G(d,p))	Jasper et al. ¹⁵³ (B3LYP/6-311++G(d,p))	Madden, et. al. ¹⁵⁴ (BAC-MP4)	This Work (CBS-QB3)
Fulvene + H	P2	0.00	0.00	0	0.00
Methylcyclopentadienyl	INT6	-208.78	-208.36	-209	-209.47
<i>tert</i> -Hydrofulvenyl	INT4	-112.97	-113.39	-102	-109.59
α -Hydrofulvenyl	INT7	-204.18	-203.34	-216	-208.83
β -Hydrofulvenyl	INT5	-183.26		-189	-185.11
cyclopropylcarbiny	INT3	-144.77	-143.93	-151	-144.79
cyclohexadienyl	INT2	-222.17	-221.33	-235	-226.15
Benzene + H	P1	-131.38	-130.96	-134	-135.37
H-Elimination					
[Fulvene + H $\rightleftharpoons$ INT6]		4.35		9	
[Fulvene + H $\rightleftharpoons$ INT4]	TS8	20.63	19.29	20	14.25
[Fulvene + H $\rightleftharpoons$ INT7]	TS13	8.58	4.18	9	-0.30
[Fulvene + H $\rightleftharpoons$ INT5]	TS12	9.37	6.07	8	-3.10
[INT2 $\rightleftharpoons$ Benzene + H]	TS2	-107.95	-108.37	-122	-108.55
H-Shift/Transfer					
[INT6 $\rightleftharpoons$ INT4]	TS9	20.38	-12.05	3	-11.70
[INT4 $\rightleftharpoons$ INT7]	TS10	-40.84	-40.42	-37	-41.79
[INT5 $\rightleftharpoons$ INT7]	TS11	-61.50	-60.25	-61	-63.35
Ring Opening					
[INT4 $\rightleftharpoons$ INT3]	TS7	-83.26	-82.84	-96	-89.09
[INT3 $\rightleftharpoons$ INT2]	TS6	-69.45	-69.45	-77	-74.28

Table 3.3 Comparison of the stationary points for the C₆H₇ PES involving ring expansion in methylcyclopentadiene radicals by Dubnikova and Lifshitz.¹⁵ All values are relative to cyclohexadienyl (INT2 on this PES) and reported in units of kJ/mol.

Stationary Points	Label (This PES)	Dubnikova & Lifshitz ¹⁵ (QCISD(T)//B3LYP/cc-pVDZ)	This Work (CBS-QB3//B3LYP/BSB7)
Methylcyclopentadienyl	INT6	20.29	16.68
<i>tert</i> -Hydrofulvenyl	INT4	113.51	116.56
α -Hydrofulvenyl	INT7	16.57	17.32
β -Hydrofulvenyl	INT5	37.82	41.04
cyclopropylcarbiny	INT3	88.78	81.36
cyclohexadienyl	INT2	0.00	0.00
H-Shift/Transfer			
[INT6 $\rightleftharpoons$ INT4]	TS9	225.98	214.45
[INT4 $\rightleftharpoons$ INT7]	TS10	185.06	184.36
[INT5 $\rightleftharpoons$ INT7]	TS11	166.06	162.80
Ring Opening			
[INT4 $\rightleftharpoons$ INT3]	TS7	151.00	137.06
[INT3 $\rightleftharpoons$ INT2]	TS6	165.23	151.87

It is worth noting that one transition state leading to the formation of fulvene was not located in this work but was identified using the higher-level methods by Madden et. al.¹⁵⁴ and Jasper et. al.¹⁵³ The transition state of interest pertains to the H-elimination step of INT6 to fulvene + H (see Figure 3.6). This barrier was within the error of the CBS-QB3 method used in this work (± 4.4 kJ mol⁻¹) and should be considered negligible for the purpose of this study as the barrier would be significantly small and all the computed product channels are highly exothermic relative to the reactants.

3.2.1 Cycloaddition Mechanism

Figure 3.5 Schematic of the C_6H_7 potential energy surface proceeding through CH cycloaddition onto the C=C bond of the cyclopentadiene reactant. The reaction enthalpies (300K) are given in kJ mol^{-1} for the intermediates and products relative to the reactants. The PES shows those pathways (black, green, red, and purple) included in the MESMER calculations. The light blue pathway leading to the formation of INT9 is not included in the MESMER calculations.

Figure 3.5 displays a portion of the C_6H_7 potential energy surface for the CH radical cycloaddition across C2 and C3 (C=C bond) of cyclopentadiene. The CH cycloaddition mechanism consists of two entrance channels and multiple exit channels through H-loss including those leading to the formation of cyclic products: benzene (purple), fulvene (green), and bicyclo[3.1.0]hexadiene (red). Ring-opening from INT2 leads to the formation of a linear C_6H_7 intermediate, from which more H loss pathways are revealed, and will be discussed in more detail in Section 3.2.3. Two exothermic bicyclic intermediates are formed from the CH cycloaddition

entrance channel: INT1A, for which the CH substituent is oriented towards the ring structure, and INT1B, where the CH substituent is oriented away from the ring structure. The slight structural difference between the two intermediates leads to an 0.4 kJ mol^{-1} energy difference. Isomerization from INT1A to INT1B can occur through a barrier of 7.8 kJ mol^{-1} relative to INT1B. INT1A can also undergo a ring opening through TS1 with relative energetics of 95.7 kJ mol^{-1} to form the resonance stabilized six-membered ring intermediate INT2. The formation of INT2 is energetic by $-527.7 \text{ kJ mol}^{-1}$ relatively to the reactants. Formation of INT2 is the most thermodynamically exothermic channel identified on the PES due to resonance stabilization of the radical along the π -electron system of the structure. INT2 can subsequently eliminate a hydrogen from carbon C1 through TS2 lying $117.7 \text{ kJ mol}^{-1}$ above INT2 to form benzene. The formation of benzene and a hydrogen atom is the most thermodynamically accessible pathways with a reported energy of $-432.6 \text{ kJ mol}^{-1}$ relative to the reactants. INT1B can also ring open to form the stable six-membered ring INT2 through TS4 lying at 44.1 kJ mol^{-1} above INT1B and follow the same previously mentioned hydrogen elimination pathway to form benzene. The transition state to INT2 from INT1B is 51.6 kJ mol^{-1} less than for the corresponding pathway from INT1A due to the differences in the orientation of the CH substituent.

INT1B can also undergo a 1,3-hydrogen shift from the neighboring C1 through TS5 lying $141.2 \text{ kJ mol}^{-1}$ above INT1B to form the bicyclic intermediate INT3, which has thermodynamically accessible pathways to all three of the major products on the PES. INT3 decomposes through H-loss from C2 through a barrierless dissociation channel to form the bicyclic product P3. The products, P3 and a hydrogen, have the highest energetics of the three products at $-123.3 \text{ kJ mol}^{-1}$ relatively to the reactants. INT3 can also ring expand through breaking of the bond between C2 and C3 of the five-membered ring to form the six-membered ring INT2 through TS6, lying 70.4

kJ mol^{-1} above INT2. This can ultimately lead to the formation of benzene through TS2 as previously described. The methylene-substituted cyclopentadiene INT4 can form by breaking of the bond between the bicyclic substituent and C2 of the larger ring on INT3. TS7 is 55.9 kJ mol^{-1} above INT3, and INT4 has a relative energy of $408.6 \text{ kJ mol}^{-1}$ below the reactants. INT4 can further lose the remaining hydrogen substituent on C1 through TS8 that lies $123.3 \text{ kJ mol}^{-1}$ above it to form P2, fulvene. The fulvene and a hydrogen atom product set, has a relative energy of $432.6 \text{ kJ mol}^{-1}$ below that of the reactants.

3.2.2 Insertion Mechanism

Figure 3.6 Schematic of the C_6H_7 potential energy surface proceeding through CH insertion into the C-H bonds of the cyclopentadiene reactant. The reaction enthalpies (300 K) are given in kJ mol^{-1} for the intermediates and products relative to the reactants.

Figure 3.6 shows the PES for the barrierless insertion pathways along the three possible

entrance channels to form three initial methylene-substituted intermediates: INT4, INT5 and INT7. Due to the C_{2v} symmetry of cyclopentadiene, there are three sites for the CH radical to insert into the C–H bonds of the molecule: the sp^3 carbon atom (C1) or either of the two sp^2 carbon atoms along the C=C bond (C2 or C3). Insertion of the CH radical into the C–H bond of C2 leads to INT7 with a reported energy of 509.7 kJ mol⁻¹ below the reactants. Similarly, the CH radical can insert into the C–H bond of C3 to form INT5 that is 485.9 kJ mol⁻¹ below the reactants. Both INT5 and INT7 can isomerize to each other through TS11, which is 121.1 kJ mol⁻¹ above INT5. Both INT5 and INT7 can individually undergo hydrogen elimination from the sp^3 carbon to form fulvene through low lying transition states TS12 and TS13, respectively. Insertion of the CH radical into C1 produces INT4 (highlighted in red), which also results from the ring opening of INT3 along the cycloaddition pathway as discussed in the previous section (see Figure 3.5).

INT4 is the connecting intermediate between the CH cycloaddition and CH insertion mechanisms and can follow three pathways to form fulvene: two of which involve hydrogen migration and the third involves the previously described hydrogen elimination from C1 through TS8. A 1,2-hydrogen migration can occur on INT4 to isomerize to the methylcyclopentadienyl intermediate, INT6, through TS9 which lies 96.0 kJ mol⁻¹ above INT4. From INT6, barrierless hydrogen-loss from the methyl group of the intermediate leads to the formation of fulvene. A 1,3-hydrogen migration can also occur on INT4 through a barrier of 65.8 kJ mol⁻¹ to form the C2 methylene-substituted INT7.

3.2.3 Pathways to Linear Products

Figure 3.7 Schematic of the CBS-QB3 calculated C_6H_7 potential energy surface proceeding through C-H cycloaddition across a C=C bond of cyclopentadiene and pathways leading to linear C_6H_6 isomers + H. The reaction enthalpies (300 K) are given in kJ mol^{-1} for the intermediates and products relative to the reactants. Several of the pathways are adapted from a previous publication of the C_6H_7 PES.⁹

Figure 3.7 shows the PES for the barrierless CH cycloaddition across the C=C bond of CPD leading to linear C_6H_6 isomers through H loss. The PES includes the H loss pathways for the formation of benzene (light blue) and bicyclo[3.1.0]hexa-1,3-diene (brown) as shown in Figure 6, as well as H-loss pathways⁹ for the formation of six other linear isomers: 1,2-hexadien-5-yne (red), cis-2-ethynyl-1,3-butadiene (dark blue), 1,2,4,5-hexatetraene (black), 3,4-

dimethylenecyclobutene (green), trans-1-ethynyl-1,3-butadiene (pink), and hexa-1,3-dien-5-yne (purple). Figure 8 includes the H-loss channel $\text{INT2} \rightarrow \text{TS2} \rightarrow \text{benzene} + \text{H}$ from Figure 3.5, from which the ring-opening can occur. From INT2 an H shift can occur through TS14 to form INT8, from which ring-opening occurs through TS15 to form INT9 (red pathway). INT9 is the bottleneck intermediate leading to the formation of the six linear C_6H_6 products.

INT9 can undergo direct H elimination through TS16 to form 1,2-hexadien-5-yne with reported energy of $-99.4 \text{ kJ mol}^{-1}$ relative to the reactants. In addition, INT9 can directly isomerize along three additional pathways (dark blue, pink, and black) leading to the formation of the other five isomers. The lowest barrier of these is ring closure through TS17 to form INT5 from Figure 7. INT5 can follow two isomerization pathways (dark blue and green) and ultimately undergo H elimination to form linear products 2-ethynyl-1,3-butadiene and 3,4-dimethylenecyclobutene with reported energies of -149.2 and $-171.3 \text{ kJ mol}^{-1}$, respectively.

INT9 can additionally isomerize through TS20 to form INT11, from which H elimination can occur through TS21 to form 1,2,4,5-hexatetraene (black pathway). The remaining pathway from INT9 to formation of the final two products proceeds through TS22, which is thermodynamically endothermic relative to the reactants with a reported energy of $+28.6 \text{ kJ mol}^{-1}$. Isomerization through TS22 leads to INT12, which can then directly undergo H elimination through TS23 to form 1-ethynyl-1,3-butadiene (pink pathway) or isomerize to INT15 through a low barrier TS24. From INT15, H elimination can occur to form the 1,3-hexadien-5-yne (purple pathway).

3.2.4 H Abstraction

To discuss the possibility of H-abstraction pathways, the enthalpies of reaction for the CH_2 -coproducts were calculated. Table 3.4 displays the computed enthalpies of reaction for the H-abstraction products. The abstraction of a H atom from the three sites on the cyclopentadiene

molecule leads to the formation of three isomers of cyclopentadienyl. Two of these channels, abstraction from the C2 and C3 sites, are thermodynamically unfavorable relative to the reactants. Abstraction from the C1 site results in the formation of a cyclopentadienyl moiety and a CH₂ carbene, 39.3 kJ mol⁻¹ below the reactants. H-abstraction from the C2 or C3 site also results in a cyclopentadienyl moiety but with respective relative energetics of 99.5 and 97.2 kJ mol⁻¹ above the reactants. The disparity in these relative enthalpies compared to those for the C1 abstraction can be attributed to the hybridization of the site and difference in the C–H bond lengths. Additionally, abstraction from the C1 site results in electron delocalization on the five-membered ring that lends to the overall stability of the molecule. The calculated C–H bond lengths on the sp³ hybridized C1 site were approximately 1.099 Å, compared to 1.082 Å reported for the C–H bonds on the sp² hybridized C2 and C3 sites, indicating a longer bond that helps to facilitate the H-abstraction on the C1 site. In general for CH radical reactions, H-abstraction pathways are unfavorable due to higher barriers and have not been observed experimentally for other CH radical reactions with small linear hydrocarbons.^{72,76,155,156} In the case of the CH radical reaction with propane, Ribeiro et al.⁷⁶ searched for the transition states for H-abstraction pathways but could not locate saddle points on the corresponding PES. Any attempt to locate the transition state led toward the energetically favorable CH insertion channel, leading the authors to conclude that CH is more likely to insert into a C–C or C–H bond rather than abstract a hydrogen even though the H-abstraction products were energetically accessible. A similar fate was found for the CH radical approach to the propene molecule in another study by the same authors.¹⁵⁶ The CH cycloaddition and insertion pathways are considered much more energetically favorable and thus more competitive pathways than the H-abstraction pathway, which is not included in the C₆H₇ PES for these reasons.

Table 3.4 Enthalpies of reaction (300 K) for the H-abstraction pathways of the CH + cyclopentadiene reaction.

H-Abstraction Products		$\Delta_r H$ (300 K) (kJ · mol ⁻¹)
$c\text{-C}_5\text{H}_5 + \text{CH}_2$	+ CH ₂	-39.3
$2\text{-C}_5\text{H}_5 + \text{CH}_2$	+ CH ₂	+99.5
$3\text{-C}_5\text{H}_5 + \text{CH}_2$	+ CH ₂	+97.2

3.3 Product Detection

Product detection experiments on the CH(X²Π) radical reaction with cyclopentadiene were performed using the multiplexed photoionization mass spectrometry (PIMS) apparatus at the Advanced Light Source of Lawrence Berkeley National Laboratories in Berkeley, CA. The present study provides time- and isomer-resolved detection of products in the CH(X²Π) + *c*-C₅H₆ reaction and investigates a mechanism for the formation of benzene and other C₆H₆ isomers from this reaction. Products are sampled from a flow reactor irradiated at 248 nm and held at 4 Torr and 298-373 K and detected using tunable vacuum ultraviolet (VUV) photoionization coupled to time-of-flight mass spectrometry (TOF-MS). The isomers of the C₆H₆ + H product channel are quantified by fitting the resulting photoionization spectra to experimental reference and simulated photoionization spectra.

3.3.1 Cyclopentadiene Photodissociation at 248 nm

Figure 3.8 Mass spectra integrated over the 8.3–9.8 eV photon energy and 0–80 ms kinetic time range obtained from (a) photolysis of the cyclopentadiene (C_5H_6) mixture alone in helium and nitrogen buffer gases and (b) bromoform ($CHBr_3$) and cyclopentadiene mixture in helium and nitrogen buffer gases at 4 Torr and 373 K. Negative ion signals indicating depleting species are truncated.

Figure 3.8 displays mass spectra recorded upon photolysis of CPD (a) without and (b) with bromoform. The mass spectra were integrated over the energy range of interest (8.3–9.8 eV) and kinetic time of 0–80 ms. The absorption cross section of CPD was previously reported as $4.5 \times 10^{-18} \text{ cm}^2$ at 248 nm,¹⁵² and the molecule is known to readily photodissociate at this wavelength.¹⁵⁷ The depletion of CPD (m/z 66) is evident in both spectra from the negative signal displayed in the mass spectra. The depletion of the ^{13}C

isotopologue of the cyclopentadiene reactant at m/z 67 is also visible in the mass spectra. Although only a portion of the depletion is shown in Figure 3.8, the intensity ratio of the two masses supports the assignment of m/z 67 as the singly substituted ^{13}C isotopologue.

Figure 3.9 Normalized kinetic traces obtained from cyclopentadiene photolysis at 248-nm at (a) m/z 39 and (b) m/z 65. The ion signal is integrated over the 8.3–9.8 eV energy range.

Analysis of the 248-nm photodissociation of cyclopentadiene allows to directly account for photoproducts and their secondary reactions. From Figure 3.8(a), two primary products are identified through peaks appearing at m/z 39 and 65. Figure 3.9 displays the kinetic traces of

photoproducts a) m/z 39 and b) m/z 65. The shapes of the traces in Figure 10 are consistent with the formation of a radical by the laser pulse indicated by the fast rise at the photolysis laser and exponential decay thereafter. The signal at m/z 65 corresponds to the formation of cyclopentadienyl ($c\text{-C}_5\text{H}_5$) arising from the H abstraction channel of cyclopentadiene reactant. The formation of cyclopentadienyl is also confirmed by the ionization energy onset of m/z 65 at ~ 8.4 eV and from reference photoion spectra obtained by Savee et al.¹¹ and Hansen et al.¹⁵⁸ as shown in Figure 11. Another prominent peak at m/z 64, also visible in Figure 3.8, suggests the formation of C_5H_4 species: ethynylallene, methyldiacetylene and pentatetraene. These species are identified by fitting their absolute reference spectra to the experimental photoion spectrum as shown in Figure 3.10.¹⁵⁹ The m/z 64 products are likely to be the result of H_2 loss from the cyclopentadiene reactant and have been previously reported in CPD photolysis studies.^{111,160}

Figure 3.10 Photoion spectra of m/z 64 (purple triangles) and m/z 65 (black circles) obtained at 4 Torr and 373 K. The data at m/z 64 are fit (black lines) with the photoion spectra of ethynylallene ($50\pm 2\%$), pentatetraene ($4\pm 1\%$) and methyldiacetylene ($46\pm 2\%$).¹⁰ The data at m/z 65 are fit with

the cyclopentadienyl radical reference spectrum¹¹ along with contributions from m/z 64 products (ethynylallene, pentatetraene and methyldiacetylene) to account for their ^{13}C contributions.

The shape of the photoionization spectrum of C_5H_4 (m/z 64) in Figure 3.10 is also noticeable in the experimental m/z 65 spectrum, supporting the assignment of a portion of the m/z 65 signal to the $^{13}\text{CC}_4\text{H}_4$ isotopologue of m/z 64, formed from CPD photolysis. The resonantly stabilized radical propargyl (C_3H_3) is identified at m/z 39 by its ionization energy onset at ~ 8.65 eV and through comparison of the recorded photoionization spectrum with reference spectra.¹⁶¹ The corresponding kinetic time trace in Figure 3.9(a) displays a fast rise and slower exponential decay that is consistent with the formation of a resonantly stabilized radical. The vinyl radical (C_2H_3) is also observed at m/z 27 as a propargyl radical coproduct.¹¹¹ The vinyl radical is expected to be much more reactive than the resonantly-stabilized propargyl radical and thus accumulate in lower concentrations than those reported for m/z 39. This is supported by a comparatively faster decay time in the m/z 27 kinetic trace, as shown in Figure 3.11. A small amount of ion signal at m/z 27, corresponding to the vinyl radical (C_2H_3), is observed experimentally but not included in the mass range of Figure 3.8(a) due to a comparably low intensity. Lower intensity peaks are observed at m/z 38, 40, 52, 54, and 63 that are indicative of other cyclopentadiene photodissociation channels. The photodissociation products further react to form larger mass secondary products, such as those

observed at m/z 68, 76, 78, 80, 82, 90, and 92. Further insight into the m/z 78 photoproducts will be provided in Section 3.3.4.

Figure 3.11 Normalized kinetic trace of m/z 27 from the 248 nm photolysis of cyclopentadiene. The ion signal is integrated over the 8.3–9.8 eV energy range.

The mass spectrum for the CH + cyclopentadiene reaction, shown in Figure 3.8(b), is integrated over the 0–80 ms kinetic time and 8.3–9.8 eV photon energy range. Through comparison with Figure 3.8(a), the relative intensity of the peaks corresponding to the cyclopentadiene photoproducts do not significantly change upon addition of bromoform to the flow. The only exception arises in the mass of interest, m/z 78, where the intensity is 18 times greater in the presence of CH radical precursor. This increase in ion signal can be attributed to C_6H_6 cations as a result of the reaction of interest: $CH + C_5H_6 \rightarrow C_6H_6 + H$.

3.3.2 CH + Cyclopentadiene

Figure 3.12 Mass spectra (m/z 35–150) integrated over the 8.3–9.8 eV photon energy and 0–80 ms kinetic time ranges obtained from (a) photolysis of the cyclopentadiene (C₅H₆) mixture alone in helium and nitrogen buffer gases and (b) bromoform (CHBr₃) and cyclopentadiene mixture in helium and nitrogen buffer gases at 4 Torr and 373 K. Insets in the spectra show close-ups of the peaks over mass range 90–124 to examine the reaction of cyclopentadienyl photoproducts with molecular Br as discussed in the paper (m/z 93/95/106/108/118/120).

Photodissociation of bromoform at 248 nm effectively produces the $\text{CH}(\text{X}^2\Pi)$ radical through a two-photon process.^{62,162} In addition to the radical of interest, it is also known to form CHBr_2 , CHBr , Br , and Br_2 species, which can subsequently react with other photoproducts and give rise to higher mass signals as shown in Figure 3.12. The reaction of cyclopentadienyl with molecular bromine results in the appearance of peaks at m/z 144/146. Relatively less intense peaks also appear at m/z 106/108 and 118/120 from vinyl and propargyl radical reactions with atomic Br to form $\text{C}_2\text{H}_3\text{Br}^{79}/\text{C}_2\text{H}_3\text{Br}^{81}$ and $\text{C}_3\text{H}_3\text{Br}^{79}/\text{C}_3\text{H}_3\text{Br}^{81}$, respectively (inserts in Figure 3.12). Small peaks appear at m/z 93/95, resulting from single photon 248 nm photolysis of bromoform, confirming the presence of $\text{CH}_2\text{Br}^{79}/\text{CH}_2\text{Br}^{81}$ formed through H atom reactions with CHBr photoproducts. Identification of these photoproducts are further supported by their radical-like temporal profiles and confirm the presence of CHBr singlet carbene species. The small relative intensity of the peaks and temporal profiles at m/z 92/94 indicates very low yields of this photoproduct, which is in agreement with previous studies of 248 nm photolysis of bromoform.¹⁶³

Figure 3.13 Normalized kinetic trace of m/z 78 obtained by reaction of $\text{CH}(\text{X}^2\Pi)$ radical with cyclopentadiene. The ion signal is integrated over the 8.3–9.8 eV energy range.

Figure 3.13 shows the normalized kinetic time trace of the m/z 78 ion signal with the addition of bromoform in the flow. The observed rise of the m/z 78 temporal profile has a corresponding k_{1st} value of $\sim 860\text{ s}^{-1}$ observed through exponential fits to the data. The k_{1st} value for the observed rise of photoproduct m/z 65 is $\sim 8700\text{ s}^{-1}$ and is faster in comparison to the k_{1st} value ($\sim 450\text{ s}^{-1}$) for the m/z 78 kinetic trace obtained from the photolysis of CPD alone. Once the m/z 78 products are formed, a slight increase in signal continues over the kinetic time range. This has been observed in a previous CH radical study¹⁶⁴ and can likely be attributed to divergence of the laser beam along the flow tube that leads to a gradient in the initial CH radical number density. It is also worth noting that a small peak at m/z 79 appears in the mass spectrum from the title reaction as well, which is consistent with ^{13}C contribution from the C_6H_6 product. The lack of a temporal decay that would be expected for a free radical in the kinetic trace of the m/z 79 product further rules out any contribution from stabilization of a C_6H_7 radical intermediate.

Based on the comparison between the two mass spectra in Figure 3.8 and the discussion above, formation of m/z 78 through H-elimination seems to be the only observed CH + CPD product channel. Because of cyclopentadienyl formation by 248 nm photodissociation of cyclopentadiene, we avoid drawing any conclusions on the contribution from the abstraction channel $\text{CH} + \text{C}_5\text{H}_6 \rightarrow \text{CH}_2 + \text{C}_5\text{H}_5$.

3.3.3 m/z 78 Isomer Products

Figure 3.14 shows the m/z 78 photoionization spectra for (a) CPD alone and (b) CPD + CHBr_3 at 4 Torr and 373 K. Both spectra are integrated over 0–80 ms after the photolysis pulse and are the result of an individual measurement. Each photoion spectrum is reported with error

bars calculated from twice the shot noise in the number of detected ion counts ($2\sqrt{N}$). To remove the contribution of C_6H_6 signal that arises only from the $C_5H_6 +$ laser interaction, we subtract the m/z 78 spectrum in Figure 3.14(a) from the m/z 78 spectrum obtained when $CHBr_3$ is added to the system (Figure 3.14(b)). Both experiments were performed under identical conditions except that an equivalent mass flow of helium is replaced by $CHBr_3$ in the second experiment. The resulting spectrum in Figure 3.14(b) should therefore contain only the m/z 78 contributions from the $CH + C_5H_6$ reaction. The addition of bromoform to the reaction flow increases the sharp onset at 9.25 eV that is characteristic of benzene.¹⁶⁵

Figure 3.14 Photoionization spectra of m/z 78 ion signal obtained from (a) 248-nm photolysis of cyclopentadiene and (b) 248-nm photolysis of bromoform (CH radical precursor) and cyclopentadiene reactant integrated over the 0–80 ms time range (open circles) at 4 Torr and 373 K and background subtracted for CPD photolysis. The spectra are shown with error bars calculated from twice the shot noise in the number of detected ion counts ($2\sqrt{N}$). The solid red lines in both panels are a fit to the data using the absolute photoionization spectra of benzene (purple dashed line)¹² and fulvene¹³ (solid green line) as well as the integrated photoelectron spectra of six other C_6H_6 isomers: cis/trans-1-ethynyl-1,3-butadiene (solid orange line), 1,2,4,5-hexatetraene (magenta dot-dashed line), cis-2-ethynyl-1,3-butadiene (dark blue dot-dashed line), 1,2-hexadien-5-yne (light blue dashed line), and 3,4-dimethylenecyclobutene (dark green dashed line). The fitted branching fractions are displayed in Table 5 for panel (a) and Table 6 for panel (b).

Table 3.5 Structures, CBS-QB3 adiabatic ionization energies, and product branching fractions obtained by fitting the m/z 78 photoion spectrum from CPD only in Figure 3.14(a).

C_6H_6 Isomeric Product (Abbreviated Name)	Geometry	$IE_{CBS-QB3}$ (eV)	Branching Fraction (% $\pm 2\sigma$)
Benzene		9.25	46 (± 8)
Fulvene		8.36	0 (± 7)
Cis-2-ethynyl-1,3-butadiene (2E13BD)		8.93	15 (± 4)
Trans-1-ethynyl-1,3-butadiene (1E13BD)		8.62	0 (± 0)
1,2,4,5-Hexatetraene (1245HT)		8.49	4 (± 2)
Hexa-1,2-dien-5-yne (12HD5Y)		9.30	33 (± 5)
3,4-Dimethylenecyclobutene (34DMCB)		8.76	2 (± 2)
Hexa-1,3-dien-5-yne (13HD5Y)		8.64	0 (± 0)

Table 3.6 Structures, CBS-QB3 adiabatic ionization energies, and fitted product branching fractions for the m/z 78 photoionization spectrum of CPD + CHBr_3 shown in Figure 3.14(b).

C_6H_6 Isomeric Product (Abbreviated Name)	Geometry	$\text{IE}_{\text{CBS-QB3}}$ (eV)	Branching Fraction (% $\pm 2\sigma$)
Benzene		9.25	90 (± 5)
Fulvene		8.36	8 (± 5)
Cis-2-ethynyl-1,3-butadiene (2E13BD)		8.93	0 (± 0)
Trans/Cis-1-ethynyl-1,3-butadiene (1E13BD)		8.62	1 (± 2)
1,2,4,5-Hexatetraene (1245HT)		8.49	1 (± 2)
Hexa-1,2-dien-5-yne (12HD5Y)		9.30	0 (± 4)
3,4-Dimethylenecyclobutene (34DMCB)		8.76	0 (± 2)
Hexa-1,3-dien-5-yne (13HD5Y)		8.64	0 (± 3)

The spectra are fit using a least-squares fitting routine to the weighted sums of absolute photoionization data of several C_6H_6 isomers obtained from previous studies by Locklear et al.¹³, Cool et al.¹² and calculated here (see Figure 3.15). The residuals of the fitting routines on the experimental photoionization spectra were within 5% for CPD only (Figure 3.14(a)) and within

3% for CPD + CHBr₃ (Figure 3.14(b)). The selection of the C₆H₆ isomers included in the fit was based upon the ionizing energy range considered here (8.3–9.8 eV) and other reasonable products expected based on previous studies of the C₆H₆ and C₆H₇ potential energy surfaces.^{9,96,104,153,166,167} Based upon this selection criteria, the reference spectra of eight possible C₆H₆ isomers (Figure 3.15) were included in the fitted spectrum: benzene, fulvene, cis-2-ethynyl-1,3-butadiene (2E13BD), trans-1-ethynyl-1,3-butadiene (1E13BD), 1,2,4,5-hexatetraene (1245HT), 1,2-hexadien-5-yne (12HD5Y), 3,4-dimethylcyclobutene (34DMCB), and 1,3-hexadien-5-yne (13HD5Y). Within the energy resolution of the experiment (~40 meV), it is not possible to differentiate between the trans- and cis-1-ethynyl-1,3-butadiene (1,3-hexadien-5-yne) species. The C₆H₆ isomers along with their structures, CBS-QB3 calculated adiabatic ionization energies, and resulting fitted branching fractions with 2 sigma standard deviation from Figure 3.14(b) are shown in Table 3.6. Table 3.5 shows the product distributions for Figure 3.14(a) (CPD only). Although the absolute photoionization spectrum of fulvene is not shown in Figure 3.14(a), it was included in the fitting routine with a reported branching fraction of 0 (± 7) %, as shown in Table 3.5.

Figure 3.15 Absolute photoion spectra of eight C_6H_6 isomers. The Franck-Condon factors are calculated using the PESCAL program¹⁴ for six of the isomers: 3,4-dimethylenecyclobutene (red), cis-2-ethynyl-1,3-butadiene (dark blue), hexa-1,3-dien-5-yne (gold), 1,2,4,5-hexatetraene (magenta), hexa-1,2-dien-5-yne (light blue), and trans-1-ethynyl-1,3-butadiene (black). The photoion spectra for benzene (purple) and fulvene (green) are experimentally determined from the works of Cool et al.¹² and Lockyear et al.¹³, respectively.

From the fitting results, benzene is the isomer contributing the majority ($90 (\pm 5) \%$) to the CPD + CH product distribution. Fulvene, which is not detected in the case of CPD photolysis (Table 3.5), has a branching fraction of $8 (\pm 5) \%$ and is the only other cyclic isomer assigned. Very minor contributions from 1-ethynyl-1,3-butadiene ($1 (\pm 2) \%$) and 1,2,4,5-hexatetraene ($1 (\pm 2) \%$) are also reported. Fitting the photoionization spectra to only benzene and fulvene reveals no significant difference in the branching fractions reported, as shown in Figure 3.16. In addition, a minor contribution from another C_6H_6 isomer, 1,5-hexadiyne, cannot be ruled out but is not included into the experimental fits because its ionization energy onset (9.98 eV) is outside the energy range used here. Previous single-point energy calculations of 1,5-hexadiyne suggest it is thermodynamically accessible on the C_6H_7 PES.¹³⁰ However, it is not anticipated to change the

assignment of benzene as the major product in the CPD + CH reaction but rather only play a small role in the minor C_6H_6 product branching fractions. Product detection experiments of CH radical reaction with the cyclopentadiene analog, pyrrole (C_4H_4NH), further suggest that the major product is cyclic in structure.¹⁷

Figure 3.16 Photoionization spectra (open circles) of m/z 78 ion signal obtained from 248 nm photolysis of bromoform and CPD reactant integrated over the 0–80 ms time range. The solid red line is a fit to the data using the absolute photoionization spectra of benzene¹² and fulvene¹³. The dashed purple and solid green lines show the contribution of benzene and fulvene, respectively, to the fit with the included branching fractions.

3.3.4 CD + Cyclopentadiene

Figure 3.17 Mass spectra integrated over the 8.3–9.8 eV photon energy and 0–80 ms kinetic time range obtained from (a) photolysis of the bromoform (CHBr₃, black line) and CPD mixture in helium and nitrogen buffer gases and (b) deuterated bromoform (CDBr₃, blue line) and CPD mixture in helium and nitrogen buffer gases at 4 Torr and 298 K.

Figure 3.17 displays the mass spectra recorded upon 248 nm photolysis of CPD (a) with bromoform (CHBr₃) and (b) with deuterated bromoform (CDBr₃). The mass spectra were integrated over the energy range of interest (8.3–9.8 eV) and kinetic time of 0–80 ms at 298 K. Comparison of the CPD + CDBr₃ mass spectra (red line) with the CPD + CHBr₃ mass spectra (black line) shows a significant increase in m/z 79 signal relative to the m/z 78 signal. The results are consistent with the formation of a C₆H₅D species. It is also noted that the m/z 78 signal, significant of the formation of a C₆H₆ species, is non-negligible in the reaction of CDBr₃ + CPD. Figures 3.18 shows the photoionization spectra for the reaction of CDBr₃ and CPD at (a) m/z 78 and (b) m/z 79 with fits to the absolute photoionization spectra of benzene¹² and fulvene¹³. The reported branching fractions for the fits to m/z 78 in Figure 3.18(a) are 76 (± 2) % and 24 (± 1) % for benzene and fulvene, respectively. The branching fractions for m/z 79 in Figure 3.18(b) are 66

(± 2) % and 34 (± 1) % for benzene and fulvene, respectively. Further insight into the mechanisms behind the formation of C_6H_5D/C_6H_6 species are discussed further on.

Figure 3.18 Photoionization spectra (open circles) of a) m/z 78 and b) m/z 79 obtained from the 248 nm photolysis of deuterated bromoform ($CDBr_3$) and cyclopentadiene integrated over the 0–80 ms time range at 4 Torr and 298 K. The solid red lines in both panels are a fit to the data using the absolute photoionization spectra of benzene¹² (purple dashed line) and fulvene¹³ (solid green line). The fitted branching fractions for each species are displayed in the graph.

3.3.5 H-Assisted Isomerization

It is also necessary to discuss the role that H-assisted isomerization could have in the branching fraction distribution of the C_6H_6 products. Several studies of the C_6H_7 PES reveal that the exit channel barriers are low enough with respect to the $C_6H_6 + H$ products for the process to easily occur.^{130,153,166,168} However, under the experimental conditions of this work, there is very little evidence to support that H-assisted isomerization plays a major role in the formation of benzene. The fast rise in the m/z 78 temporal profiles of Figure 3.13 do not indicate the occurrence of H-assisted isomerization in the products. A comparison of the branching fractions extracted from the m/z 78 photoionization spectra integrated over various kinetic time ranges (0–4, 0–10, and 10–80 ms) also does not reveal evolution in the product isomer distribution (Figure 3.19). In fact, the branching fraction of benzene remains consistent at $90 (\pm 3) \%$ over the 0–4 ms time range in comparison to the $90 (\pm 5) \%$ reported over the 0–80 ms time range. Integrated over longer time ranges (0–10 ms and 10–80 ms) and within the error bars of the fitting routine, the benzene branching fraction remains unchanged.

Figure 3.19 Photoionization spectra (open circles) of m/z 78 ion signal obtained from 248 nm photolysis of bromoform (CH radical precursor) and cyclopentadiene reactant integrated over the a) 0 – 4 ms, b) 0 – 10 ms, and c) 10 – 80 ms time ranges and background subtracted for C₆H₆ contribution from cyclopentadiene photolysis at 4 Torr and 373 K. The solid red line is a fit to the data using the absolute photoionization spectra of benzene¹² and fulvene¹³ as well as the integrated photoelectron spectra of six linear C₆H₆ isomers: cis-2-ethynyl-1,3-butadiene (2E13BD), trans-1-ethynyl-1,3-butadiene (1E13BD), 1,2,4,5-hexatetraene (1245HT), 1,2-hexadien-5-yne (12HD5Y), 3,4-dimethylenecyclobutene (34DMCB), and hexa-1,3-dien-5-yne (13HD5Y). The fitted branching fractions are displayed in each graph.

3.4 Master Equation Calculations

To better understand the role of the cycloaddition reaction mechanism for formation of benzene, RRKM-based Master Equation (ME) calculations using the open-source software MESMER¹⁴⁶ have been performed on a portion of the C₆H₇ PES shown in Figure 3.5. The light blue pathway INT2→TS14→INT8→TS15→INT9 is not included in the MESMER calculations because the intermediates and transition barriers are expected to be less accessible relative to the pathways leading to the formation of cyclic products, likely due to high energy barriers ($\Delta E=317.8$ kJ mol⁻¹ and $\Delta E=171.2$ kJ mol⁻¹) and entropic factors due to ring opening, as shown in Figure 8. The barrierless formation of the bicyclic product (red pathway) is omitted as well. The PES used for the MESMER calculations is displayed in Figure 3.20.

Figure 3.20 Potential energy surfaces used in MESMER for the cycloaddition (a) and insertion (b) mechanisms. The energies are ZPE energies (0K) calculated using CBSQB3 in kJ mol⁻¹.

3.4.1 CH Cycloaddition

The PES used for the MESMER calculations is displayed in Figure 3.20(a). In the ME calculation, the reaction is presumed to proceed through CH cycloaddition across one of the two symmetrically equivalent C=C bonds to give INT1A with a rate coefficient set to the experimental one.¹³⁰ The reactant number densities are chosen from the experimental conditions. The intermediates INT1A and INT1B are found to be in equilibrium. Two cyclic C₆H₆ products from the PES are considered in the ME analysis: benzene and fulvene. The ME analysis is run for temperatures ranging from 300 K to 1000 K and pressures ranging from 5 Torr to 760 Torr in both Ar and N₂ as buffer gas. Benzene is found to be the sole cycloaddition product (>99%) over the considered pressure and temperature ranges. Sensitivity analyses are performed to investigate the effect of model input parameters on the benzene population. The energy transfer parameter (ΔE_{down}) is varied from 100 to 800 cm⁻¹ while the Lennard-Jones parameters ε and σ are varied from 300 to 600 cm⁻¹ and 2 to 6 Å, respectively. Over these ranges, the final modeled benzene population is found to be independent of temperature and pressure and the initial input parameters.

Figure 3.21 RRKM theory calculated microcanonical rate constants for the unimolecular isomerization and dissociation of the C_6H_7 reaction intermediates. The energy origin is set to INT2.

Figure 3.21 displays the microcanonical rate constants calculated using RRKM theory for the unimolecular isomerization and dissociation of the reaction intermediates. Following INT1 formation by cycloaddition of the CH radical (INT1A and INT1B are in equilibrium), isomerization occurs very rapidly through ring opening to form INT2. The H-shift pathway that competes with this process, converting INT1 to bicyclic INT3, is calculated to be several orders of magnitude slower than the ring opening path to INT2 and considered unfavorable relative to expansion to a 6-member ring. Additionally, the isomerization of INT2 to bicyclic INT3 through TS6 ($\Delta E=151 \text{ kJ mol}^{-1}$) is relatively slow, being on the same order of magnitude as the $\text{INT1B} \rightarrow$

TS5→*INT3* H-shift pathway ($\Delta E=142.1$ kJ mol⁻¹). Based on the PES in Figure 3.5, the formation of fulvene + H through cycloaddition can only proceed through the 3-member ring opening of the bicyclic *INT3* to *INT4* followed by H elimination through *TS8*. Overall, the most important kinetic competition is *INT2*→*TS6*→*INT3* (the rate limiting step to fulvene formation) vs. *INT2*→*TS2*→benzene. The latter pathway has a substantially larger rate constant at all energies. The microcanonical rates support benzene being the most energetically and entropically favorable cycloaddition product, with no fulvene formation. This comparison between experiment and theory suggests that fulvene is more likely to be formed by barrierless insertion of the CH radical into one of the C–H bonds of CPD.¹³⁰

3.4.2 CH Insertion

The PES used for the MESMER calculations is displayed in Figure 21(b). The theoretical method used here does not allow for calculation of the relative contributions between the cycloaddition and C–H insertion entrance channels nor between the three insertion channels. Nonetheless, RRKM-ME calculations are performed using the PES in Figure 3.6, not including *INT6*. Within the level of theory employed here, there is no identifiable saddle point for decomposition of *INT6* into fulvene + H. Three individual calculations are performed starting with direct formation of *INT4*, *INT5*, or *INT7*, respectively. The calculations are performed using the same parameters as for the cycloaddition calculations (Section 3.4.1). At room temperature and 5 Torr, benzene formation is found to be the dominant mechanism (85%) when starting from the formation of *INT4*. In the case of the direct formation of the insertion intermediates *INT5* and *INT7*, fulvene formation becomes dominant with branching fractions of 82% and 74%, respectively.

Figure 3.22 Calculated fulvene branching fractions for CH cycloaddition to INT1 (black) and insertion of the CH radical into one of the C–H bonds of CPD forming INT4 (red), INT5 (green), or INT7 (blue).

Figure 3.22 displays the calculated fulvene branching fractions for isolated cycloaddition or isolated C–H insertion as a function of temperature upon reaction of the CH radical with CPD to form INT1 (black), INT4 (red), INT5 (green), or INT7 (blue). Considering the maximum fulvene fraction from insertion (82% after formation of INT5), the total branching fraction of the insertion mechanism must represent at least 10% of the overall CH + CPD reaction mechanism to reproduce the measured 8% fulvene fraction. In addition, if the insertion/cycloaddition fraction doesn't change with temperature, the overall fulvene/benzene branching fraction from the CH + CPD reaction is only slightly dependent on temperature. Benzene is therefore likely to remain the main cyclic reaction product from the CH + CPD reaction at combustion temperatures with a non-negligible amount of fulvene.

3.5 Conclusions

The reaction of the $\text{CH}(\text{X}^2\Pi)$ radical with cyclopentadiene (C_5H_6) was studied extensively and through several experimental and theoretical techniques. The rate constant for the reaction was determined experimentally using PLP/LIF techniques under pseudo-first order conditions over a pressure range of 2.7–9.7 Torr and from 298–450 K. The dominant product channel for the reaction is the formation of C_6H_6 isomers + H, which is investigated using multiplexed photoionization mass spectrometry at 298–373 K and 4 Torr. To better complement the experimental studies, a combination of theoretical techniques is utilized. Calculations on the C_6H_7 potential energy surface (PES) are conducted using DFT and CBS-QB3 methods to provide further insight into the reaction mechanism. Master Equation calculations of the branching fractions using MESMER software allows for comparison with the experimentally determined product distribution. RRKM theory calculations give mechanistic insight into the unimolecular rates of isomerization and decomposition of the reaction intermediates from the PES.

In the kinetic experiments, the lack of pressure dependence and the average rate coefficient of $2.70(\pm 1.34) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K agree with the rapid, pressure independent rate coefficients found in previous studies of CH radical reactions with unsaturated hydrocarbons.^{5–7,60,74,134,169,170} The pressure independence of the measured rate coefficients together with the good exponential fits of the CH decays suggest that the reaction is already performed at or near the high-pressure limit with negligible dissociation of the initial reaction adduct. The temperature independence of the rate constants over the 298–450 K range in Figure 3.4 is in agreement with the absence of an energy barriers, which is consistent with the widely accepted mechanism of CH radical reactions with unsaturated hydrocarbons, as first proposed by Berman et al.⁵ The non-Arrhenius temperature dependence of the fast rate coefficient is likely to be due to a strongly

attractive potential driven by long-range electrostatic forces between the reactants (i.e. adiabatic capture) in agreement with Canosa et al.⁶⁰ and as discussed in the reviews of by Stoecklin et al.¹⁷¹ and Clary.¹⁷²

Using PIMS-TOF product detection techniques, the direct formation of C₆H₆ isomers by the reaction of the methylidyne radical (CH(X²Π)) with cyclopentadiene has been observed. All C₆H₆ products observed in this work are formed through elimination of an H atom. Fitting the experimental photoion spectra to C₆H₆ reference spectra reveals that the two major products from the title reaction are benzene, with a branching fraction of 90 (± 5)% and fulvene, with a branching fraction of 8 (± 5)%. Several linear isomers are found to be minor products. The findings presented here suggest a novel and competitive route to benzene formation in combustion environments rich in cyclopentadiene.

Calculations on the C₆H₇ PES were performed to complement the experimental kinetics and product detection studies. The energetics for the intermediates and transitions states in Figures 3.5 and 3.6 are in good agreement with earlier C₆H₇ PES involving the formation of benzene and/or fulvene.^{15,45,93,101,153,154,166,173} The PES calculations further support the experimentally determined rate constant for the CH radical reaction with CPD. The rate constant is fast and near the collision limit, which provides strong evidence to support barrierless CH entrance channels. Product detection experiments showing benzene forming as the major product in the reaction are further reconciled by its high exothermicity and thermodynamic favorability on the PES.

The RRKM-ME calculations remain in good agreement with the experimental data shown here. From Figure 3.17, the ratio of *m/z* 78 decreases by a factor of ~13.5 when CDBr₃ is introduced into the flow while *m/z* 79 increases by a factor of ~3.5. Fits to the photoionization spectra of the

CDBr₃ + CPD in Figure 3.18 reveal benzene as the major product in both *m/z* 78 and 79 pathways. The *m/z* 78 benzene product can be attributed to the CH insertion mechanism through formation of INT4 undergoing a ring closure to INT3. The increase in *m/z* 79 ion signal from Figure 3.17 is supported by a 10% increase in the branching fraction of fulvene from Figure 3.16. Although some discrepancy remains from the CDBr₃ + CPD data, it is important to note that most of the product shifts to *m/z* 79. The uncertainty in the branching fractions of Figure 3.16 and the mass spectra of Figure 3.17 lie in the branching fractions of the entrance channels, which cannot be fully determined in the current experiment.

Most studies of CH reacting with unsaturated closed-shell hydrocarbons conclude that cycloaddition across a C=C bond dominates, with little evidence that CH inserts into C–H bonds.^{68,69,174,175} In the present work, the experimental observation of fulvene is inconsistent with the Master Equation calculations including only cycloaddition, whereas two of the three C–H insertion pathways form mostly fulvene in our calculations. It is therefore possible to conclude that the insertion mechanism accounts for at least 10% of the overall CH + CPD mechanism to support the experimentally derived product branching fractions. Master Equation calculations that properly treat the competition between the barrierless CH + CPD entrance channels are substantially more difficult but would provide further information of the competitiveness of the insertion mechanisms relative to the cycloaddition mechanism. The experimental product branching fractions and mechanistic information are significant in exploring alternative and competitive routes to the formation benzene in carbon-rich gas phase environments.

3.6 References

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Chapter 4: CPD + OH Radical Reaction

The reaction of combustion-relevant hydrocarbons with the OH radical could lead to the formation of intermediate resonantly stabilized radical structures containing a hydroxyl group. The formation of OH-containing adducts proceeds through the initial formation of a van der Waals (VDW) complex that can isomerize to an addition intermediate. Evidence of such adducts has been suggested in previous studies of OH initiated oxidation studies with aromatic molecules.¹⁻⁷ In the kinetic study of the OH radical with fulvenallene, the H abstraction mechanism is believed to dominate at temperatures above 500 K.⁶ The formation of a VDW complex and stabilization of a RSR adduct is believed to be the primary mechanism up to 500 K due to low energy barriers of formation. Due to the structural similarities between the fulvenallene and cyclopentadiene reactant, both containing a five member ring, a similar mechanism can be expected for the OH reaction with CPD at low temperatures.

4.1 Potential Energy Surface Calculations

To infer information about the intermediates and products of the OH radical reaction with CPD, the enthalpy of reaction (300 K) was calculated using DFT and CBS-QB3 methods, as described in Section 2.3.1. The reaction mechanism of the OH radical with unsaturated hydrocarbons can proceed through three pathways: abstraction of an H atom, association to the Π system, and addition to a carbon.

Figure 4.1 shows the structures and computed reaction enthalpies (300 K) at the CBS-QB3 level of theory for the expected products from the OH radical reaction with CPD. Figure 4.1 only shows the eight possible OH intermediates and products at this level of theory. The OH radical can abstract from any of the three carbon sites on CPD to produce the cyclopentadienyl (CPDyl)

radical + H₂O. All the abstraction products are exothermic relative to the reactants; however, where the H atom abstraction occurs ultimately affects the stability of the CPDyl radical and thus the energetics. If OH abstracts from the C(2) or C(3) site along the C=C bond, then the resulting CPDyl structure have reported energies of -13.7 and -16.0 kJ mol⁻¹, respectively. Abstraction from the sp³ hybridized C(1) site forms a CPDyl radical that is resonantly stabilized compared to the abstraction from the sp² sites and has relative reported energy of -152.5 kJ mol⁻¹. The other two thermodynamically accessible intermediates result from the addition of the OH radical to a sp² carbon. The energies are exothermic relative to the reactants for these species: 2-C₅H₆OH at -167.5 kJ mol⁻¹ and 3-C₅H₆OH at -109.0 kJ mol⁻¹. The H loss channels following addition are endothermic relative to the reactants. There are three H-atom loss co-products: 1-C₅H₅OH at +41.3 kJ mol⁻¹, 2-C₅H₅OH at +9.3 kJ mol⁻¹, and 3-C₅H₅OH at +3.2 kJ mol⁻¹.

Figure 4.1 Schematic of the CBS-QB3 calculated C₅H₆OH potential energy surface proceeding through OH reaction with CPD. The reaction enthalpies (300 K) are given in kJ mol⁻¹ and are relative to the reactants. The numbering in front of the structures refers to the carbon site of CPD where the reaction is occurring.

Identification of such an adduct could result from the barrierless formation of a van der Waal's complex.⁸⁻¹⁰ Higher level calculations were used to further investigate the pathways to the formation of 2-C₅H₆OH and 3-C₅H₆OH. Figure 4.2 shows the schematic of part of the C₅H₆OH potential energy surface proceeding through OH reaction with CPD and focusing on the formation of the OH addition intermediates. The ZPE energies are given in kJ mol⁻¹ and are relative to the reactants. The ZPE were calculated at the CCSD(T)/cc-pVTZ and the geometry of the structures optimized at the M06-2X/6-311++G**level of theory. Figure 4.2 shows the barrierless formation of a van der Waal's (VDW) complex at -41.7 kJ mol⁻¹ through OH association with the CPD molecule. The VDW complex can further stabilize to form the addition intermediates through two low lying transition state barriers, TS1 (-36.6 kJ mol⁻¹) and TS2 (-28.4 kJ mol⁻¹). OH addition at the C(2) site proceeds through TS1 and forms 2-C₅H₆OH with a reported energy of -194.3 kJ mol⁻¹. While OH addition at the C(3) site proceeds through TS2 and forms 3-C₅H₆OH with a reported energy of -143.2 kJ mol⁻¹.

Figure 4.2 Schematic of the $\text{C}_5\text{H}_6\text{OH}$ potential energy surface proceeding through OH reaction with CPD and focusing on the m/z 83 intermediate. The ZPE energies are given in kJ mol^{-1} and are relative to the reactants. The PES was calculated at the CCSD(T)/cc-pVTZ//M06-2X/6-311++G** level of theory. The numbering in front of the structures refers to the carbon site of CPD where the reaction is occurring.

4.2 Product Detection

Product detection experiments on the OH(X²Π) radical reaction with cyclopentadiene (C₅H₆) were performed using the multiplexed photoionization mass spectrometry (PIMS) apparatus at the Advanced Light Source of Lawrence Berkeley National Laboratories in Berkeley, CA. The experiment provides time- and isomer-resolved detection of products, as well as intermediate species, in the OH(X²Π) + *c*-C₅H₆ reaction. CPD reactant is prepared through thermal cracking of the dimer DCPD and the vapor is collected in a cylinder with He buffer gas to obtain the desired concentration, as previously described.^{11,12} The OH(X²Π) radical is generated from 248 nm photolysis of the hydrogen peroxide precursor (H₂O₂) by a KrF excimer laser (R1).¹³

A mechanism for the formation of a stabilized intermediate species of *m/z* 83 (2-C₅H₆OH) is investigated. The species of interest are sampled from a flow reactor irradiated at 248 nm and at 4 Torr and 298 K. The stabilized intermediate is identified through investigation of resulting mass spectra and fitting the photoionization spectra to simulated reference spectra.

4.2.1 CPD + OH Mass Spectrum

Figure 4.3 displays the mass spectra recorded upon 248 nm photolysis of CPD (a) without and (b) with OH radical precursor, hydrogen peroxide. The mass spectra were obtained at 8.2 eV and integrated over the 0–70 ms kinetic time range. The absorption cross section of CPD was previously reported as $4.5 \times 10^{-18} \text{ cm}^2$ at 248 nm,¹⁴ and the molecule is known to readily photodissociate at this wavelength.¹⁵ The photoproducts of CPD at 248 nm has been discussed in Section 3.3.1 and only briefly reviewed here. In Figure 4.3(a), the photodissociation of CPD at 8.2 eV gives rise to photoproducts of *m/z* 80 and 92. These masses were also identified in previous studies of the CH radical reaction with cyclopentadiene. It is important to note in Figure 4.3(a) that

no visible peaks appear for the masses of interest, m/z 82 and 83. Upon addition of H_2O_2 to the flow at 8.2 eV in Figure 4.3(b), two prominent peaks appear at m/z 82 and 83. These peaks can be attributed to the reaction of $\text{OH} + \text{CPD}$. The m/z 82 signal is likely the formation of $\text{C}_5\text{H}_5\text{OH}$ species through an association complex that initially forms through a van der Waal's complex of m/z 83, as shown in Figure 4.2. The formation of m/z 82 will proceed through the formation of intermediate m/z 83 species ($\text{C}_5\text{H}_6\text{OH}$); however, a lower intensity peak observed at m/z 83 indicates the detection of this stabilized intermediate $\text{C}_5\text{H}_6\text{OH}$ species. A small portion of the m/z 83 peak intensity ($\sim 5.5\%$) comes from the ^{13}C isotopologue of the m/z 82 $\text{C}_5\text{H}_5\text{OH}$ species.

Figure 4.3 Mass spectra obtained at 8.2 eV photon energy and integrated over 0–70 ms kinetic time range obtained from 248 nm photolysis of (a) cyclopentadiene mixture alone in helium and buffer gases and (b) hydrogen peroxide (H_2O_2) and cyclopentadiene mixture in helium and nitrogen buffer gases at 4Torr and 298 K.

The CPD molecule has two sites across the C=C bond for OH addition to occur, as shown in Figures 4.1 and 4.2. Table 4.1 shows the potential C₅H₅OH and C₅H₆OH isomers along with their CBS-QB3 calculated ionization energies. The numbering at the front of the formula indicates which carbon site of CPD the OH has reacted with.

Table 4.1 Structures and CBS-QB3 calculated adiabatic ionization energies for the *m/z* 82 and 83 species of the reaction of OH radical with CPD.

Formula	Mass (g/mol)	Name	Molecule	IE (ev) CBS-QB3
1-C ₅ H ₅ OH	82.10	Cyclopenta-2,4-dien-1-ol		8.65
2-C ₅ H ₅ OH	82.10	Cyclopenta-1,3-dien-1-ol		7.82
3-C ₅ H ₅ OH	82.10	Cyclopenta-1,3-dien-2-ol		8.10
2-C ₅ H ₆ OH	83.10	Cyclopentenyl-2-ol		7.28
3-C ₅ H ₆ OH	83.10	Cyclopentenyl-3-ol		6.67

Figure 4.4 Mass spectrum integrated over the 7.2–7.6 eV photon energy and 0–70 ms kinetic time range obtained from the 248 nm photolysis of CPD + H₂O₂ in helium and nitrogen buffer gases at 4 Torr and 298 K.

Figure 4.4 shows the 248 nm photolysis of CPD + H₂O₂ over the 0–70 ms kinetic time range at 4 Torr and 298 K. The mass spectrum was integrated over the 7.2–7.6 eV photon energy range to remove the contribution of m/z 82 ¹³C isotopologue in the ion signal. The prominent peak in Figure 4.4 arises at m/z 83, while there is no discernable m/z 82 ion signal in the spectrum. This agrees with the ionization energies in Table 4.1 for the H elimination products of m/z 82. Since no m/z 83 peak was observed in the CPD only mass spectrum of Figure 4.3(a), the m/z 83 ion signal in Figure 4.4 must come from the OH radical reaction with CPD. The kinetic trace for m/z 83 from 248 nm photolysis of CPD + H₂O₂ over the 7.2–7.6 eV photon energy range is shown in Figure 4.5. The shape of the trace in Figure 4.5 is consistent with the formation of a radical species. The sharp rise in ion signal at laser pulse $t=0$ indicates formation from the photolysis laser, while the fast, exponential decay within ~5 ms is indicative of a reactive radical species.

Figure 4.5 Normalized m/z 83 kinetic trace obtained from 248 nm photolysis of CPD + H₂O₂ integrated over the 7.2–7.6 eV photon energy range.

The 2-C₅H₆OH intermediate has a calculated ionization energy of 7.28 eV while the 3-C₅H₆OH species is reported at 6.67 eV (Table 4.1). To distinguish between the identity of the OH addition isomers, the m/z 83 photoionization spectrum was examined. Figure 4.6 shows the m/z 83 photoionization spectrum obtained from 248 nm photolysis of cyclopentadiene with H₂O₂. The spectrum is integrated over the 0–70 ms time range at 4 Torr and 298 K and background subtracted for the ~5.5% contribution of the ¹³C isotopologue of m/z 82. The solid red line is a fit to the data using the integrated photoionization spectrum of 2-C₅H₆OH calculated in this work. It is clear from inspection of the onset of the ion signal in Figure 4.6 that the m/z 83 contribution over the 7.2–7.6 eV energy range is solely the result of the 2-C₅H₆OH species. There is no indication of ion signal before ~7.3 eV in Figure 4.6 that would indicate the presence of the 3-C₅H₆OH species.

Figure 4.6 Photoionization spectrum of m/z 83 ion signal obtained from 248 nm photolysis of cyclopentadiene with H_2O_2 . The spectrum is integrated over the 0–70 ms time range at 4 Torr and 298 K and background subtracted for the $\sim 5.5\%$ contribution of the ^{13}C isotopologue of m/z 82. The solid red line is a fit to the data using the integrated photoionization spectrum of 2- $\text{C}_5\text{H}_6\text{OH}$ calculated in this work.

4.3 Conclusions

The reaction mechanism of the $\text{OH}(\text{X}^2\Pi)$ radical with cyclopentadiene was studied through experimental product detection experiments complemented a theoretical investigation of the potential energy surface. This work seeks to identify the resonantly stabilized radical intermediates in the reaction of $\text{OH} + \text{CPD}$. The mass spectra from the product detection experiments (Figure 4.3 and 4.4), the formation of a m/z 83 intermediate was observed from the OH radical addition to the sp^2 hybridized carbon sites of cyclopentadiene. The kinetic trace in Figure 4.5 confirms the reactive radical nature of the m/z 83 species. Examination of the m/z 83 photoionization spectrum in Figure 4.6 supports the sole formation of 2- $\text{C}_5\text{H}_6\text{OH}$. Although there is a slight contribution ($\sim 5.5\%$) to the m/z 83 signal from the ^{13}C isotopologue of m/z 82, most of the signal can be

attributed to the OH addition on CPD mechanism. Calculations of the PES further support the identity of 2-C₅H₆OH in the *m/z* 83 ion signal, as it is the most thermodynamically accessible intermediate in Figure 4.1 with a reported energy of -167.5 kJ mol⁻¹, relative to the reactants. Higher level theory calculations on the PES also identify the barrierless formation of a pre-reactive van der Waal's complex which likely stabilizes through small transition state barriers to form the OH addition products of interest here. There is sufficient evidence to suggest the formation of a stabilized intermediate in the OH radical reaction with cyclopentadiene.

4.4 References

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Chapter 5: Concluding Remarks

Understanding the reaction of reactive species that lead to the formation of polycyclic aromatic hydrocarbons (PAHs) is essential in improving the efficacy of models that seek to study these processes in carbon-rich environments. The research presented in this dissertation provides experimental and theoretical insight into the reactions of cyclopentadiene with CH and OH radical species, three abundant molecules in combustion environments.

5.1 CH + Cyclopentadiene

The reaction of the $\text{CH}(\text{X}^2\Pi)$ radical with cyclopentadiene (C_5H_6) was studied extensively and through several experimental and theoretical techniques. The rate constant for the reaction was determined experimentally using PLP/LIF techniques under pseudo-first order conditions over a pressure range of 2.7–9.7 Torr and from 298–450 K. The dominant product channel for the reaction is the formation of C_6H_6 isomers + H, which is investigated using multiplexed photoionization mass spectrometry at 298–373 K and 4 Torr. To better complement the experimental studies, a combination of theoretical techniques is utilized. Calculations on the C_6H_7 potential energy surface (PES) are conducted using DFT and CBS-QB3 methods to provide further insight into the reaction mechanism. Master Equation calculations of the branching fractions using MESMER software allows for comparison with the experimentally determined product distribution. RRKM theory calculations give mechanistic insight into the unimolecular rates of isomerization and decomposition of the reaction intermediates from the PES.

5.2 OH + Cyclopentadiene

The reaction mechanism of the $\text{OH}(\text{X}^2\Pi)$ radical with cyclopentadiene was studied through experimental product detection experiments complemented a theoretical investigation of the

potential energy surface. This work seeks to identify the resonantly stabilized radical intermediates in the reaction of OH + CPD. The mass spectra from the product detection experiments (Figure 4.3 and 4.4), the formation of a m/z 83 intermediate was observed from the OH radical addition to the sp^2 hybridized carbon sites of cyclopentadiene. The kinetic trace in Figure 4.5 confirms the reactive radical nature of the m/z 83 species. Examination of the m/z 83 photoionization spectrum in Figure 4.6 supports the sole formation of 2-C₅H₆OH. Although there is a slight contribution (~5.5%) to the m/z 83 signal from the ¹³C isotopologue of m/z 82, the majority of the signal can be attributed to the OH addition on CPD mechanism. Calculations of the PES further support the identity of 2-C₅H₆OH in the m/z 83 ion signal, as it is the most thermodynamically accessible intermediate in Figure 4.1 with a reported energy of -167.5 kJ mol⁻¹, relative to the reactants. Higher level theory calculations on the PES also identify the barrierless formation of a pre-reactive van der Waal's complex which likely stabilizes through small transition state barriers to form the OH addition products of interest here. There is sufficient evidence to suggest the formation of a stabilized intermediate in the OH radical reaction with cyclopentadiene.

Appendix A: Cyclopentadiene Synthesis & Characterization

A. 1 Cyclopentadiene Synthesis

Scheme A.1 Thermal cracking of dicyclopentadiene into two cyclopentadiene monomers.

Cyclopentadiene is synthesized by thermal cracking of the dimer, dicyclopentadiene, as described by Moffett et. al.¹²⁹ and shown in Scheme A.1. Approximately 2–3 grams of the dicyclopentadiene starting material is heated in a 3-neck round bottom flask (RBF) containing a coiled 22-gauge 24-inch nichrome wire in the center. All the ground glass joints, and Teflon corks are sealed with high-temperature grease. The RBF is heated while the starting material is continuously stirred to approximately 180 °C at which point the nichrome wire is used to help vaporize the starting material. Nitrogen gas flows through the RBF to help carry the monomer vapor through a 30-cm long water-cooled condensing column set at 50.0 °C, the boiling point of the cyclopentadiene. The monomer material is collected in a glass bubbler in a liquid nitrogen trap. After all the starting material has been vaporized, the bubbler and collection lines are sealed off and vacuumed to remove any impurities. The bubbler is removed from the liquid nitrogen trap and opened to an empty gas cylinder. The bubbler is placed in a dewar of room temperature water to aid in the transfer to the cylinder. The final pressure of cyclopentadiene gas is recorded before dilution with nitrogen buffer gas.

Table A. 1 Physical properties of the reactant, CPD product, and buffer gas.

Material	Melting Point	Boiling Point	Vapor Pressure
Argon	-308.8 °F (-189.4 °C)	-302.5°F (-185.8°C)	-
Nitrogen	-346 °F (-210 °C)	-320.4 °F (-195.8 °C)	-
Dicyclopentadiene (C ₁₀ H ₁₂)	90.5 °F (32.5 °C)	338 °F (170 °C)	1.35 mmHg (@ 20 °C)
Cyclopentadiene (C ₅ H ₆)	-130 °F (-90 °C)	102-109 °F (39-43 °C)	400 mmHg (@ 20 °C)

A.2 Cyclopentadiene Characterization

A.2.1 Liquid Phase NMR

A small portion of the liquid product is collected from the bubbler after synthesis and analyzed using ¹H NMR and ¹³C NMR . The presence of cyclopentadiene is confirmed from the resulting spectra shown below in Figures A.1 and A.2:

Figure A.1 ^1H NMR spectrum of the liquid product dissolved in CDCl_3 .

Figure A.2 ^{13}C NMR spectrum of the liquid product dissolved in CDCl_3 .

A.2.2 Gas Phase FTIR

Gas phase FTIR is used to analyze the composition of the gas phase product. A sample of the gas mixture is loaded into a 25-cm³ double-pass gas cell (Mettler Toledo) that is coupled to an FTIR spectrometer (Mettler Toledo, ReactIR ic 15). The double-pass gas cell is vacuumed down to less than 1 Torr and the mirrors are flushed with nitrogen before recording a background spectrum. The gas cell is then filled with approximately 980 Torr of product in nitrogen buffer gas. The spectra are recorded by accumulating 256 interferograms with a resolution of 4 cm⁻¹. The total spectra are baseline subtracted and averaged together.

Vibrational assignments to the spectra are carried out using assignments made by Gallinella et. al.¹⁷⁸ and simulated IR spectra. Using the Gaussian09 suite of programs, geometry optimization and vibration frequency calculations are performed using the B3LYP/CBSB7 method. For the calculated spectrum, only the fundamental modes are present while the experimental spectra show combination. The calculated frequencies are scaled by a factor of 0.9988 and shifted by 110.5 cm⁻¹ to match the observed fundamental modes of cyclopentadiene in the experimental spectra as shown in Figure A.3. A comparison of all the values as well as the vibrational mode assignments can be found in Table A.2.

Mode	Assignment	Observed (cm ⁻¹)	B3LYP/CBSB7 (cm ⁻¹)	Gallinella, 1967 ¹⁷⁸ (cm ⁻¹)
A ₁ v ₁	CH Stretching (in-phase)			
A ₁ v ₂	CH Stretching		3083	
A ₁ v ₃	CH ₂ Stretching	2895	2908	2895
A ₁ v ₄	C=C Stretching	1508	1510	1505
A ₁ v ₅	CH Bending			
A ₁ v ₆	CH ₂ Scissoring	1381	1379	
A ₁ v ₇	CH Bending	1375	1366	1370
A ₁ v ₈	Ring			
A ₁ v ₉	Ring			
A ₁ v ₁₀	Ring			910
A ₂ v ₁₁	CH ₂ Twisting			
A ₂ v ₁₂	CH Bending			
A ₂ v ₁₃	CH Bending			
A ₂ v ₁₄	Ring Bending			
B ₁ v ₁₅	CH Stretching			3115
B ₁ v ₁₆	CH Stretching			3055
B ₁ v ₁₇	C=C Stretching	1590	1594	
B ₁ v ₁₈	CH Bending + Ring	1295	1286	1295
B ₁ v ₁₉	CH Bending + Ring	1243	1239	1242
B ₁ v ₂₀	CH ₂ Wagging	1092	1091	1091
B ₁ v ₂₁	Ring + CH Bending	961	957	961
B ₁ v ₂₂	Ring Bending	807	809	807
B ₂ v ₂₃	CH ₂ Stretching	2915	2928	2913
B ₂ v ₂₄	CH Bending			923
B ₂ v ₂₅	CH ₂ Rocking	894	903	895
B ₂ v ₂₆	CH Bending (in-phase)	663	675	664
B ₂ v ₂₇	Ring Bending			350
B ₁	v ₁₃ + v ₂₄	1625		1624
B ₂	v ₂₇ + v ₆	1729		1729
B ₁	v ₁₂ + v ₂₄	1843		1843
B ₂	v ₂₆ + v ₇	2035		2036
B ₁	v ₂₀ + v ₈	2205		2202
B ₂	v ₂₅ + v ₇	2264		2265
B ₁	v ₂₁ + v ₄	2464		2461
A ₁	v ₆ + v ₇	2749		2750

Table A.2 Vibrational assignments of the observed gas phase cyclopentadiene absorption bands.

Figure A.3 Overlay of the simulated spectrum (B3LYP/CBSB7 method) of cyclopentadiene against the experimental baseline subtracted absorption spectrum of the CPD/Ar mixture. The simulated spectrum is scaled by a factor of 0.9988 and shifted by 110.5 cm^{-1} to match the experimentally observed normal modes of CPD.