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Title

Thermal Decomposition Mechanisms of Cyclopentane, Cyclohexane, and Cycloheptane by Flash Pyrolysis Time-of-Flight Mass Spectrometry

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Abstract

Acknowledgments

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Introduction

Cycloalkanes are molecules containing three or more carbon atoms in their ring structure, many of which can be found in heavy oils such as motor fuel, natural gas, petroleum gas, kerosene, and diesel. The pyrolysis, or thermal decomposition induced by heat at high temperatures, of cycloalkanes is an important process routinely used in the chemical industry to yield many forms of hydrocarbon products. Additionally, the thermal decomposition of cycloalkanes is important in combustion, as cycloalkanes decompose upon exposure to heat or an ignition source by various pathways. Details of cycloalkane pyrolysis mechanisms have been elusive due to the highly reactive nature of the radicals produced upon thermal decomposition, and their numerous potential decomposition pathways.[4] Herein, early stage fragmentation pathways of cyclopentane, cyclohexane, and cycloheptane were studied by a flash pyrolysis vacuum ultraviolet photoionization time-of-flight mass spectrometry (VUV-PI-TOF-MS) instrument constructed in this laboratory.

Hypothesis

Isomerization between a biradical and alkene species was preliminarily observed in early pyrolysis stages of cyclohexane, and is likely a crucial intermediate to subsequent decomposition steps. Under flash pyrolysis, the cyclopentane and cycloheptane systems were predicted to undergo a ring opening pathway via cleavage of a carbon-carbon bond yielding a biradical molecule as observed in the cyclohexane system. Subsequent thermal decomposition steps will be analyzed by mass spectrometry techniques to assess for isomerization of the biradical and alkene species from the cyclopentane and cycloheptane systems.
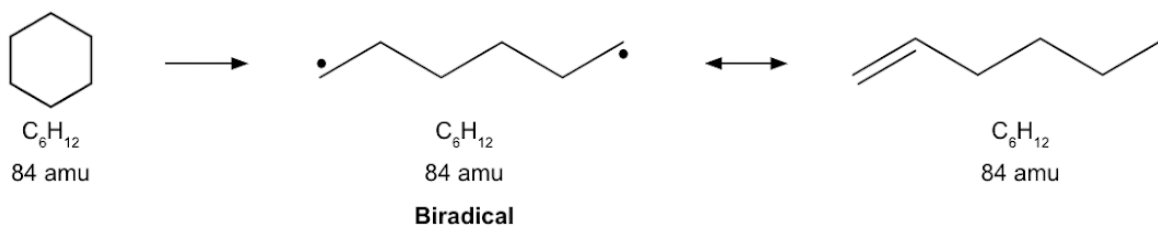
Figure I: Primary decomposition pathway of cyclohexane system was previously observed to proceed by a ring opening mechanism yielding to isomerization of the biradical and alkene species.
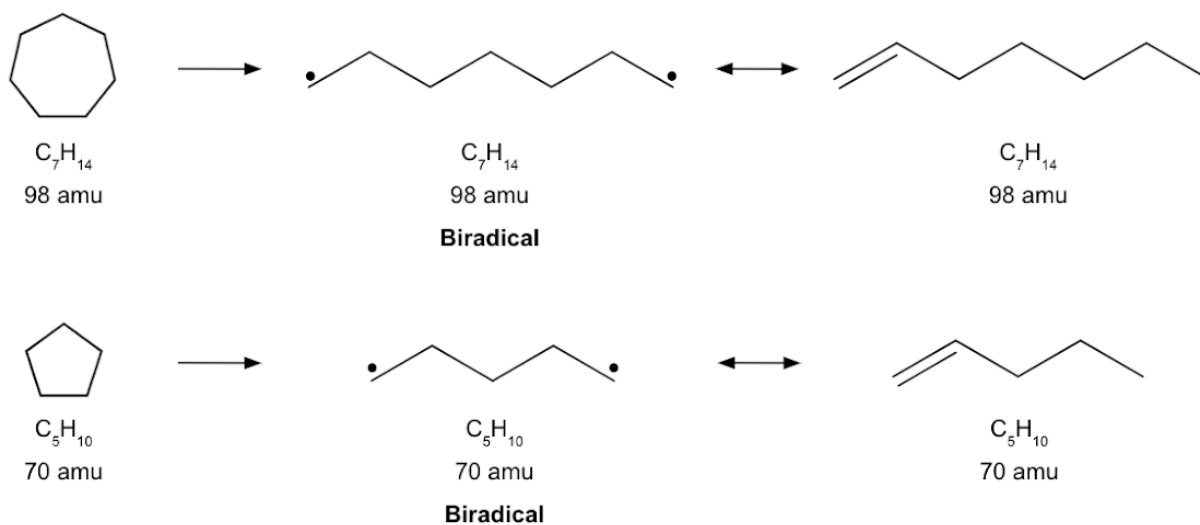
Figure II: Ring opening mechanisms and biradical to alkene species isomerization were predicted to occur in the cyclopentane and cycloheptane systems.

Methods

Cyclohexane standard (99%), cyclopentane (99%), cycloheptane (99%) samples were obtained from Sigma-Aldrich and were used without further purification. Respectively, the samples were diluted to approximately 1% concentration in Helium gas (He(g)) by passing the inert He(g) carrier gas through the liquid samples contained in glass bubblers. Analyte molecules diluted in

He(g) were then expanded into vacuum through a SiC nozzle (Carborundum Corp.) of inner diameter 1.0 mm attached to a machined alumina piece and mounted to a pulse valve (General Valve, Series 9) with orifice diameter 0.75mm operating at 10 Hz and 200 µs pulse width.[5] The sample traveled into the pyrolysis source (modeled from Chen et al. (1992)[3]) where it was exposed to temperatures ranging from 298K to 1360K so as to induce thermal decomposition of the cycloalkane systems. The fast flow through the heated region allowed for detection and analysis of short thermal decomposition reaction times. Subsequent fragments produced in the pyrolysis region underwent supersonic expansion which cooled the reactive intermediates as they expand into a vacuum. A skimmer then isolated fragments from free expansion into the photoionization region of a Wiley-Mclaren class linear time-of-flight mass spectrometer obtained from R.M. Jordan Corporation (model D-651) allowing for resolution of 200 at m/e = 150.[7] Fragments were ionized by 118 nm (10.5 eV) VUV radiation produced by tripling the frequency of the 355 nm output of a Nd:YAG (neodymium-doped yttrium aluminum garnet; $Nd:Y_3Al_5O_{12}$) laser in a low pressure Xenon gas (Xe(g)) cell (~30 Torr) attached directly to the vacuum chamber. The 118 nm radiation was focused by an MgF_2 lens through a small aperture into the photoionization region. Spectra were collected on a digital storage oscilloscope (Tektronix TDS3032, 300 MHz) using LabView software and were averaged from 512 laser shots.[5]
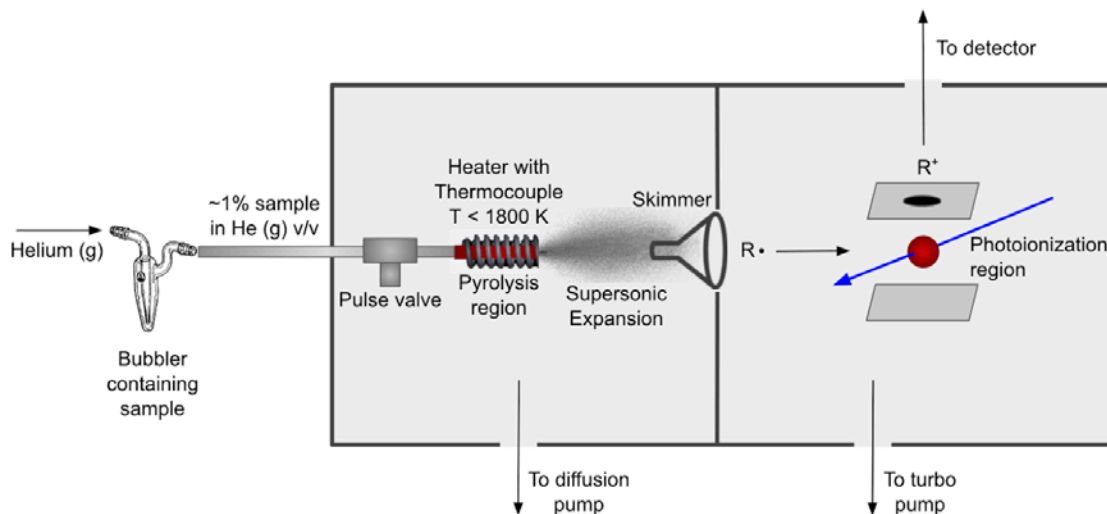
Figure III: General Schematic of VUV - SPI - TOF - MS Instrumentation

Results

TOF spectra denote the total time a given ionized fragment takes to travel from the photoionization region, through the flight path (a constant length measure), and to the detector. TOF spectra were collected for cyclopentane and cycloheptane, respectively, then TOF data was converted to generate MS spectra by classical physics relationships outlined in the following section.
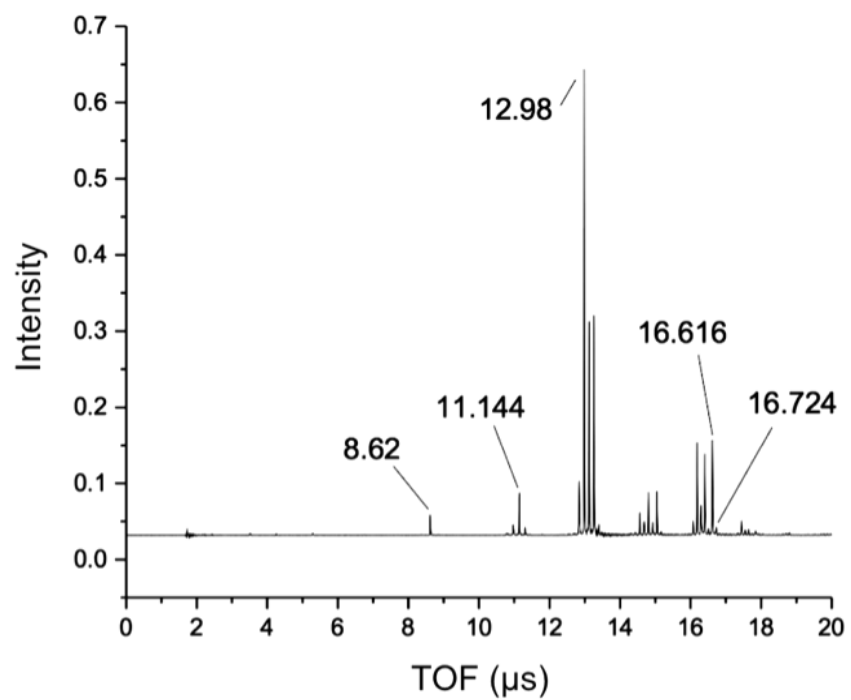
Figure IV: Cyclopentane TOF Spectrum
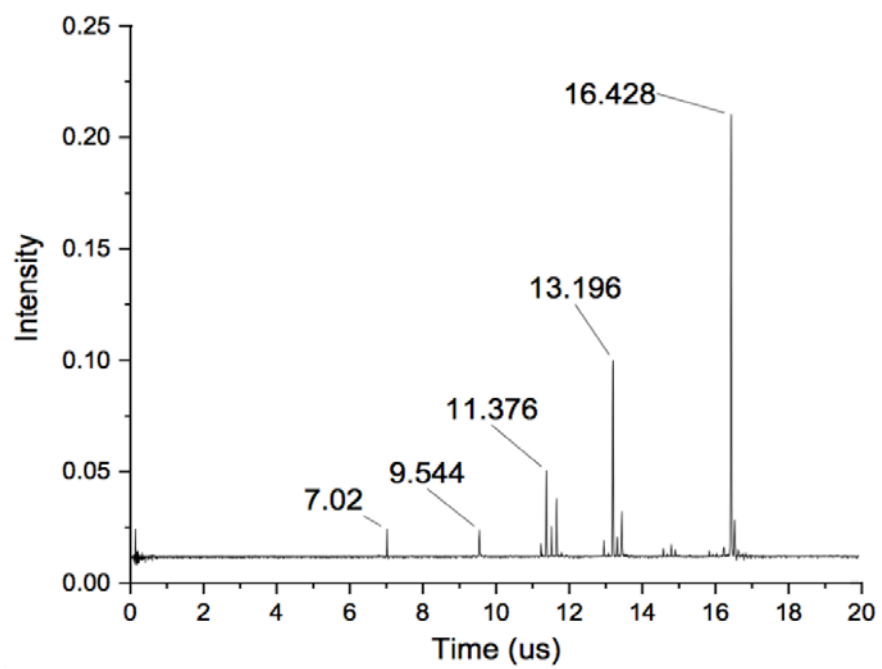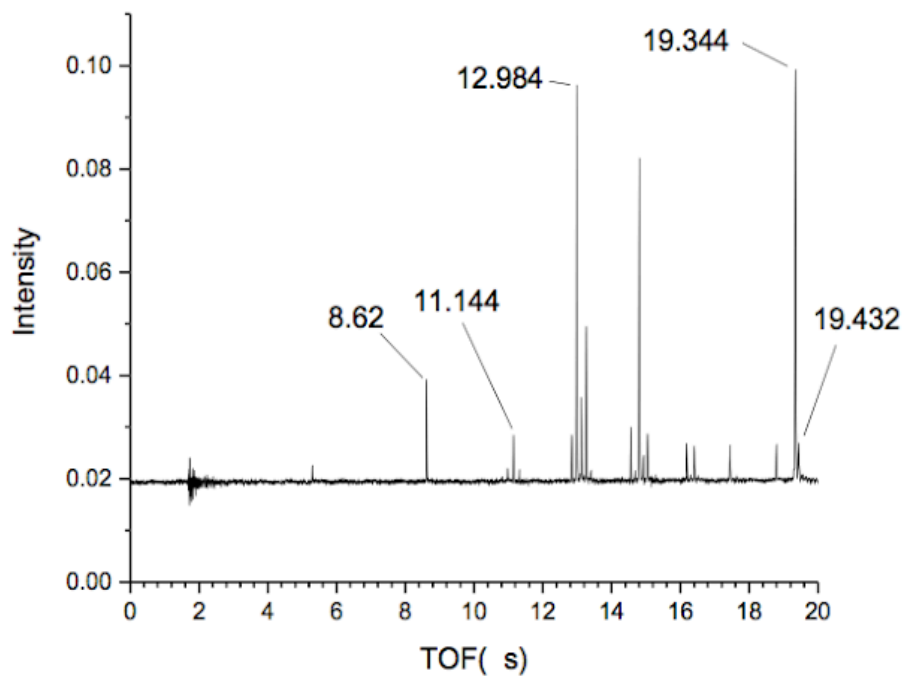

Figure V: Cyclohexane TOF Spectrum

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Figure VI: Cycloheptane TOF Spectrum
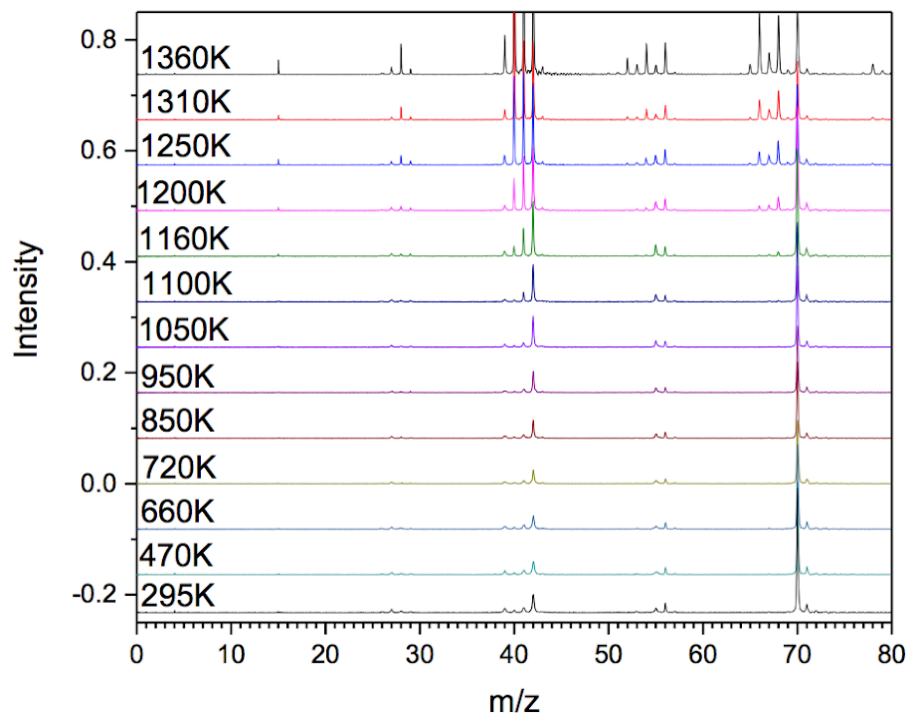
Figure VII: Cyclopentane MS Spectra Stack Plot
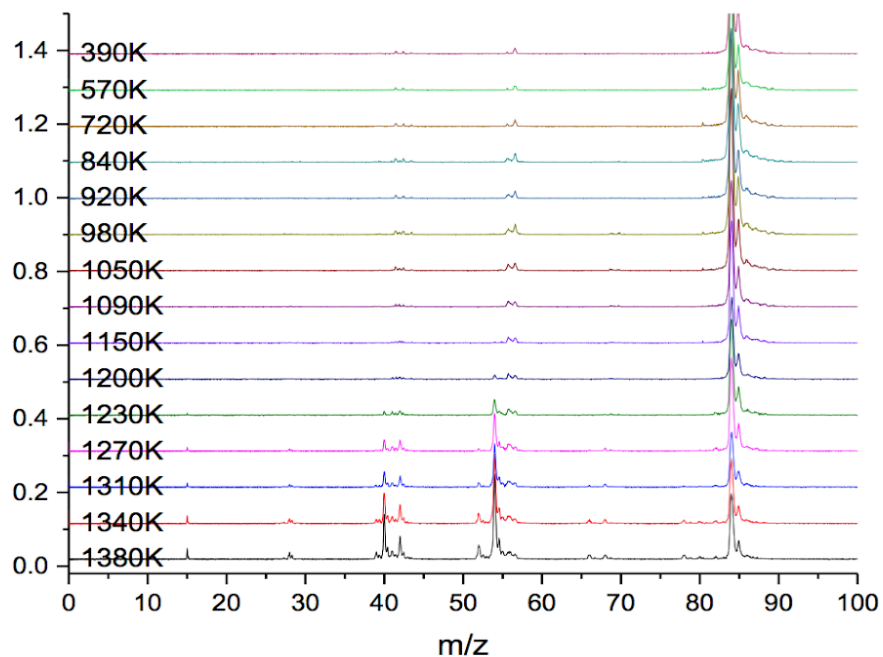
Figure VIII: Cyclohexane MS Spectra Stack Plot
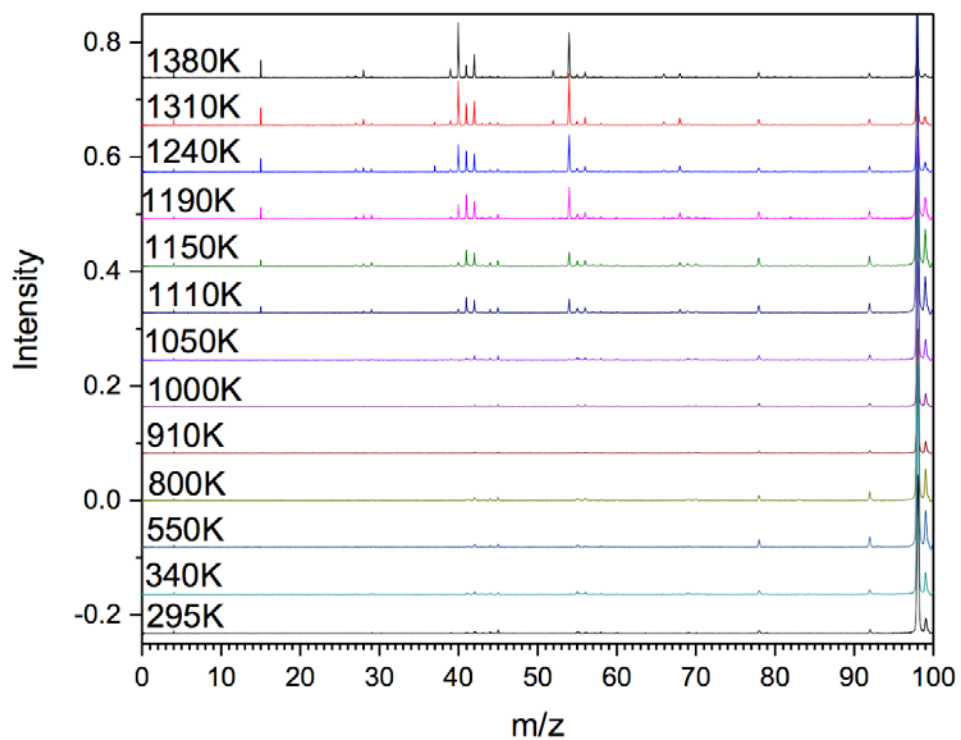
Figure IX: Cycloheptane MS Spectra Stack Plot

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TOF to MS Calculations
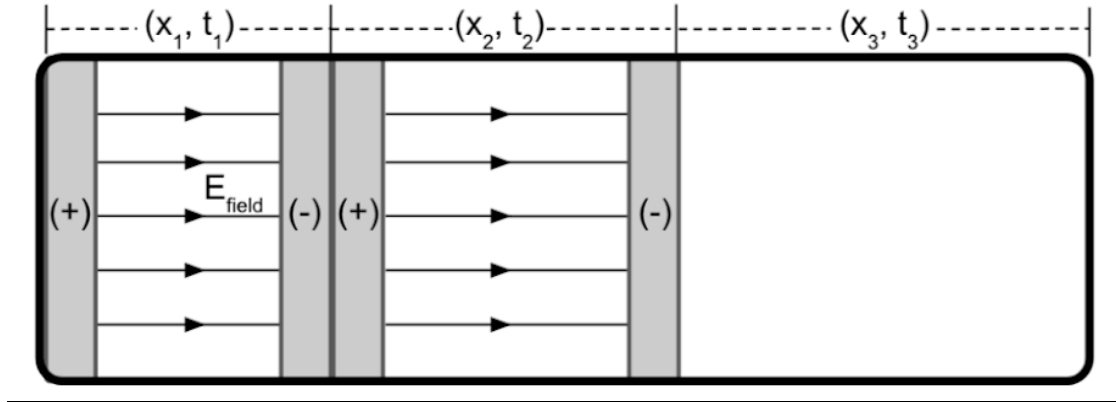
Figure X: General schematic of the flight path.

Acceleration region (t_1 and t_2)

$$F = ma = qE$$

$$x_1 = \frac{1}{2}at_1{}^2$$

$$x_1 = \frac{1}{2}qEt_1{}^2$$

$$x_1 = \left(\frac{2mx_1}{qE}\right)^{\frac{1}{2}}$$

Constant velocity region (t_3)

$$v = \frac{x_3}{t_3} \rightarrow t_3 = \frac{x_3}{v}$$

$$W_{net} = \frac{1}{2}mv^2$$

$$= Fx_2 = qEx_2$$

$$v = (\frac{2qEx_2}{m})^{\frac{1}{2}}$$

$$\rightarrow t_3 = \frac{x_3}{v} = x_3(\frac{m}{2qEx_2})^{\frac{1}{2}}$$

Total TOF

$$t_{total} = t_1 + t_2 + t_3$$

$$= \sqrt{m} \left(\sqrt{\frac{2x_1}{qE}} + x_2\sqrt{\frac{1}{2qEx_1}} + x_3\sqrt{\frac{1}{2qEx_2}} \right)$$

$$\therefore t_{total} \propto \sqrt{m}$$

Discussion
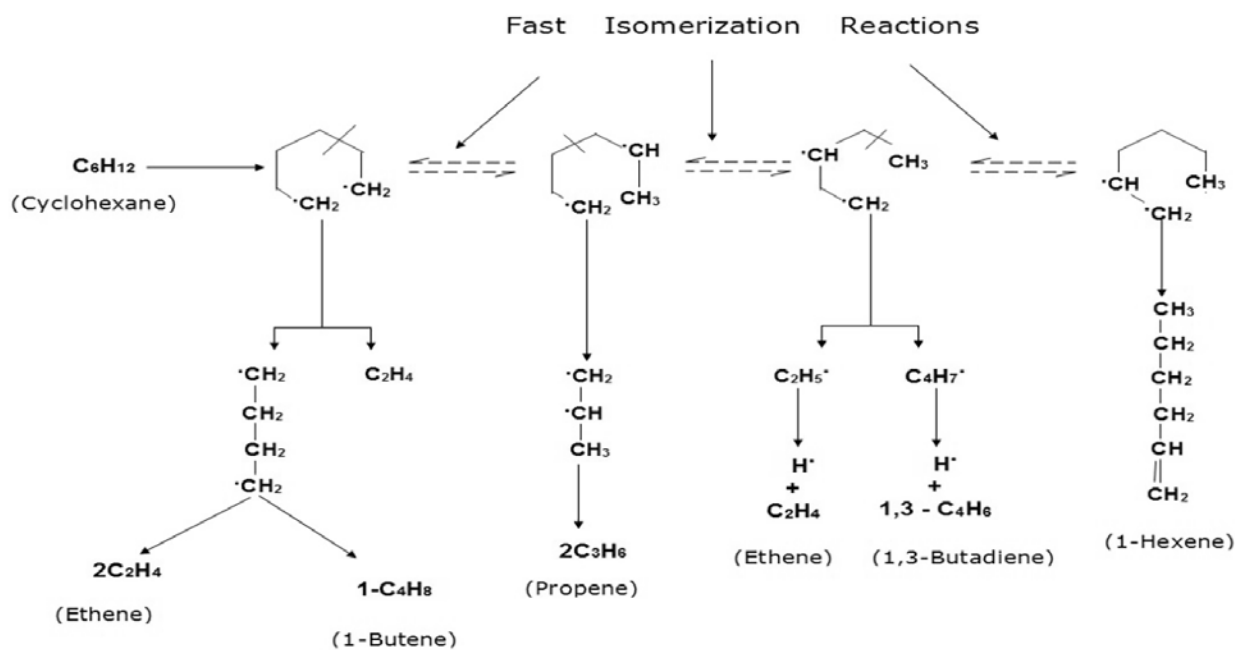
Scheme I: Thermal Decomposition Mechanism of Cyclohexane[1, 2, 3]

Cyclohexane is a reproducible system to study because it is the most stable cycloalkane system

due to the tetrahedral molecular geometry (bond angles ~109.5°) of the bonded atoms in the ring

which minimizes torsional strain; therefore, cyclohexane is a reliable quantitative kinetic model when determining the thermal decomposition pathways of other cycloalkanes such as the cyclopentane and cycloheptane systems assessed in the present study. The well-understood pyrolysis mechanism of cyclohexane reveals that the ring first opens through a carbon-carbon cleavage to yield a biradical species which quickly isomerizes between the biradical and 1-hexene: both of which provide unique avenues for secondary decomposition pathways.
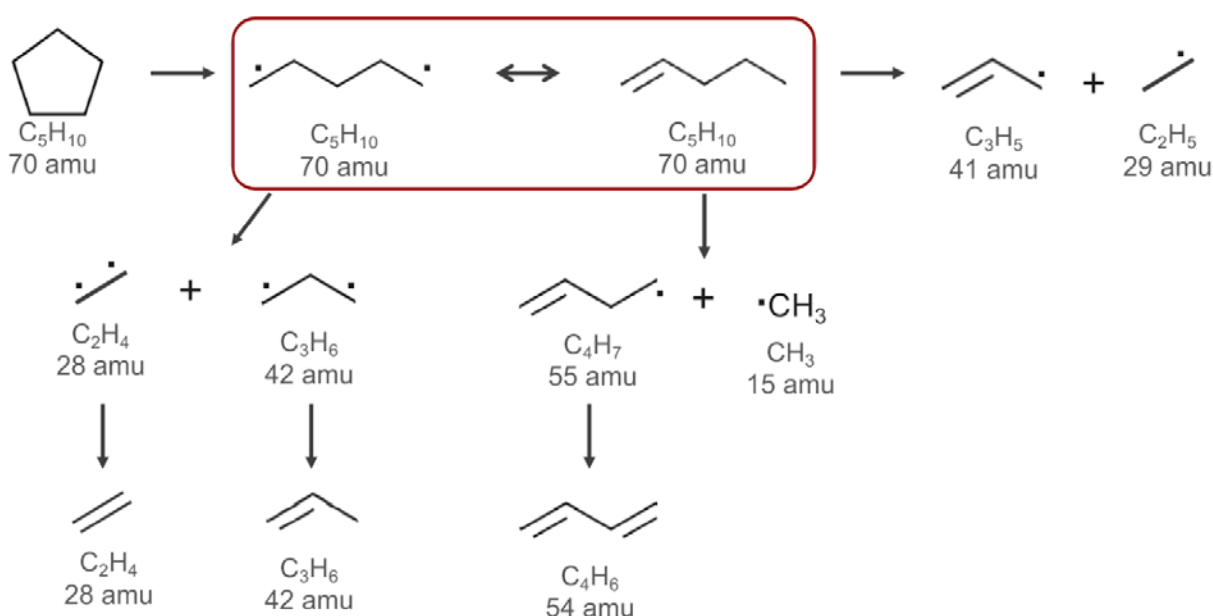

C_5H_{10}
70 amu

C_5H_{10}
70 amu

C_5H_{10}
70 amu

C_3H_5
41 amu

C_2H_5
29 amu

C_2H_4
28 amu

C_3H_6
42 amu

C_4H_7
55 amu

CH_3
15 amu

C_2H_4
28 amu

C_3H_6
42 amu

C_4H_6
54 amu

Scheme II: Proposed Cyclopentane Thermal Decomposition Mechanism

The mass spectra data of cyclopentane exhibited a decrease in intensity of the parent peak (mass-to-charge ratio (m/z) 70 amu) and a concurrent increase in the intensities of fragments as the reaction temperature was increased which allowed for the early stages of the decomposition mechanisms to be assessed. From the parent peak of 70 amu, it was hypothesized that a biradical intermediate which isomerizes into 1-pentene would be produced via carbon-carbon bond cleavage. The formation of the biradical species was confirmed by the identification of 28 amu

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and 42 amu fragments which could only be produced by the thermal decomposition of the

biradical precursor and not of the 1-pentene intermediate as depicted in *Scheme II*. A conjugated

1,3-butadiene (m/z = 54 amu) was found to be produced through the loss of a methyl group in

the 1-pentene precursor. Additionally, 1-pentene was a precursor for the formation of allylic (m/z

= 41 amu) and ethyl radicals (m/z =29 amu). Cyclohexane and cycloheptane were found to have

similar dissociation patterns as cycloheptane as they all were found to decompose as

hypothesized through the formation of a biradical species and alkene isomer intermediates. Some

fragments may not have been detected if their ionization energy was higher than the photon

energy of the laser.
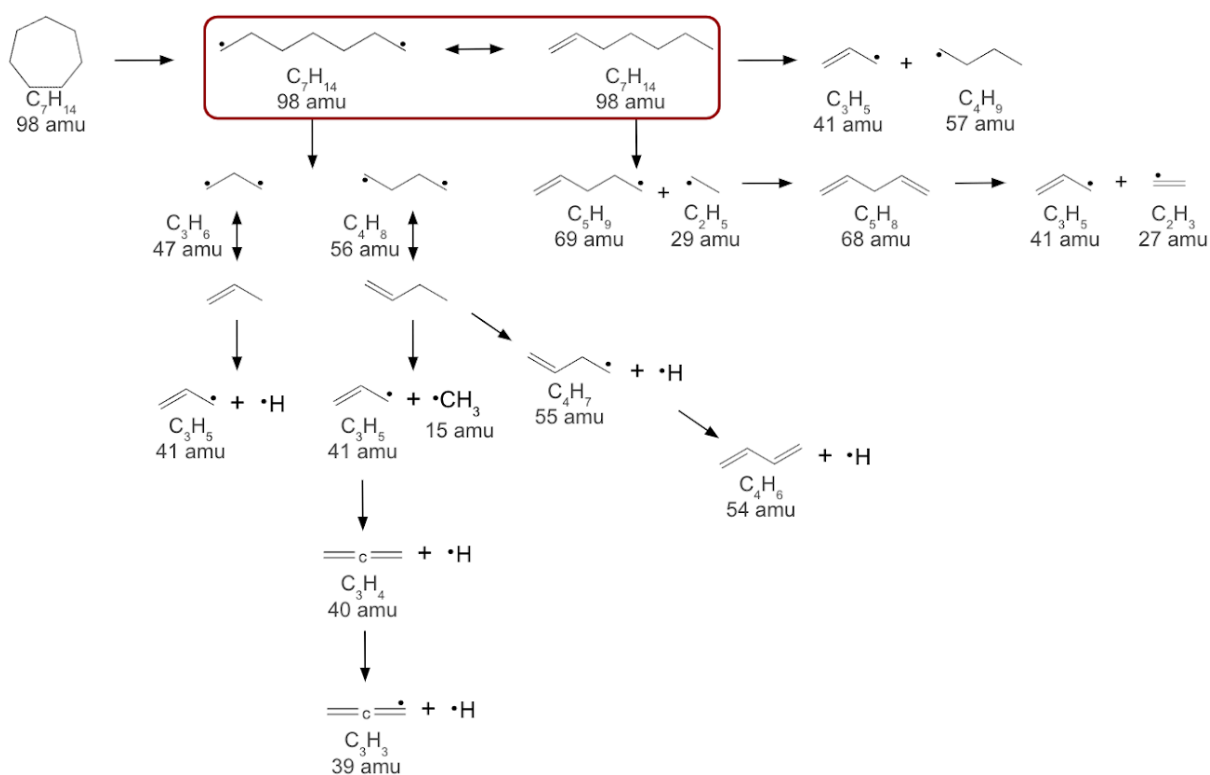
Scheme III: Proposed Cycloheptane Thermal Decomposition Mechanism

The cycloheptane system was the most difficult system to study as the ring is larger and thus can create fragments via more thermal dissociation channels than cyclopentane and cyclohexane; however, by focusing on the early decomposition steps, a comparison could be made between the cycloheptane system and the cyclohexane system. As the reaction temperature was increased, the intensity of the parent peak (m/z = 98 amu) decreased consistently in the cycloheptane mass spectra data which was consistent with the cyclohexane and cyclopentane. The isomerization between the biradical species and 1-heptene in the cycloheptane pyrolysis mechanism was confirmed by the identification of 47 amu and 56 amu fragments which are produced in the early stages of cycloheptane pyrolysis and could only be produced by the thermal decomposition of the biradical precursor and not of the 1-heptene intermediate as depicted in *Scheme III*. Additionally, the 15 amu fragment, which corresponds to the loss of a methyl radical, was observed to increase in intensity on the mass spectra for the cycloheptane system, and as depicted in *Scheme III*, the 15 amu fragment is a product of the thermal decomposition of the biradical species and not the 1-heptene intermediate. Fragments 29 amu and 69 amu were produced in the early decomposition stages but are products only of the 1-heptene intermediate which reinforces the fast isomerization between the biradical species and 1-heptene in a pyrolysis reaction.

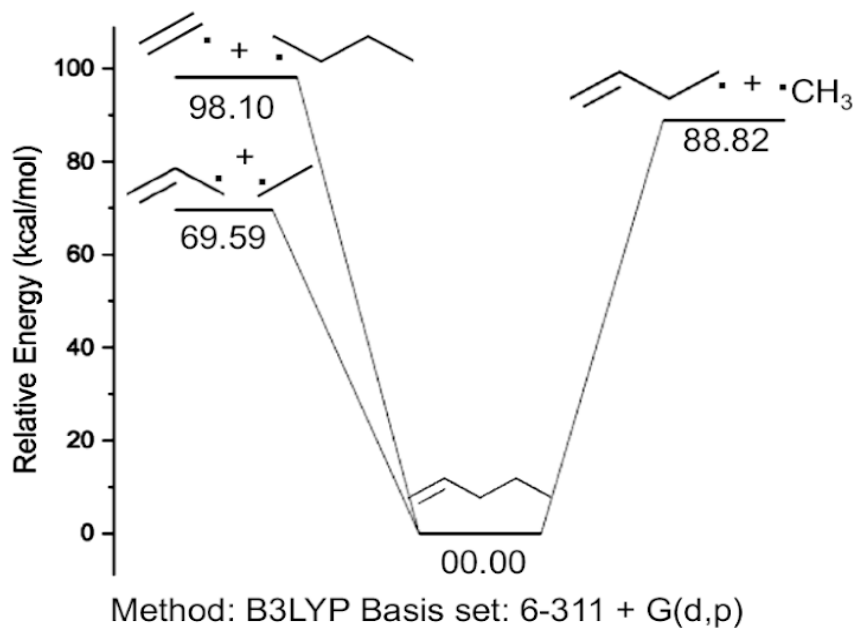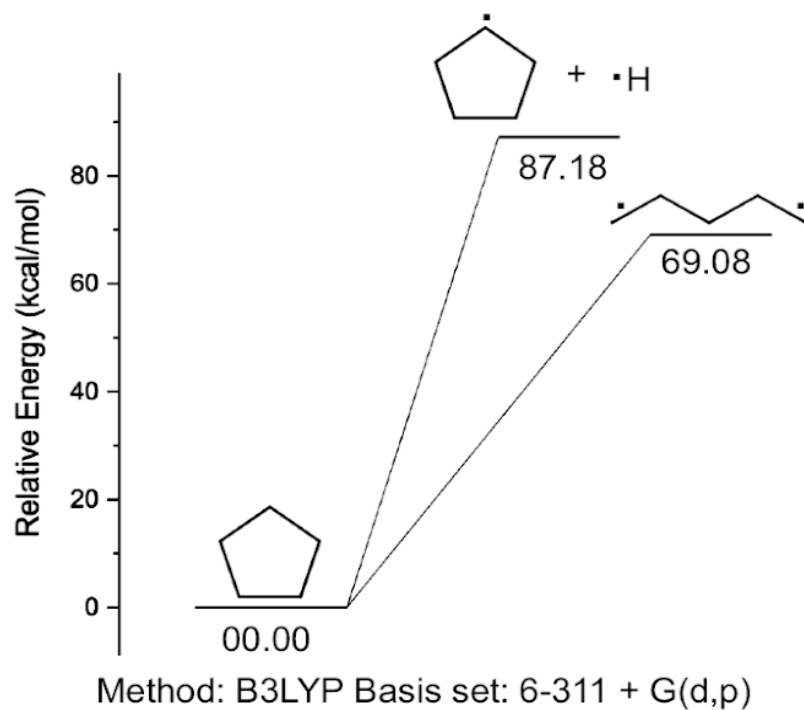Potential Energy Diagrams of Cyclopentane

Figure XI: Sample potential energy diagrams of proposed cyclopentane dissociation channels.

The potential energy diagrams in *Figure XII* depict the relative potential energy of each proposed thermal decomposition pathway. The data obtained by GaussView DFT energy computation helps to identify the most probable dissociation channels, and thus allowing for the construction of the pyrolysis mechanisms for cyclopentane, cyclohexane, and cycloheptane systems. Dissociation by certain pathways is highly unlikely due to energetic barriers such as the dissociation of cyclopentane into hydrogen radical and cyclopentane radical illustrated in *Figure*. The biradical species under study corresponds to stable energetic values, and thus is a highly stable intermediate present in the early stages of thermal decomposition for cyclopentane, cyclohexane, and cycloheptane.

Next Steps

Subsequent experimentation will expand the thermal decomposition evaluation of cycloalkanes to halogenated cycloalkane systems to assess the decomposition of cycloalkyl radicals upon cleavage of the halogen - carbon bond when the system is heated.

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