A shock tube laser schlieren study of cyclopentane pyrolysis

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Table 1: $(28+2)*7.6*2 = 456$

Fig. 1: $[(5.36*25.4)+10]*2.2*2 + 149 = 788$

Fig. 2: $[(3.65*25.4)+10]*2.2 + 60 = 286$

Fig. 3: $[(2.28*25.4)+10]*2.2 + 31 = 180$

Fig. 4: $[1.92*25.4)+10]*2.2 + 64 = 193$

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Abstract

The dissociation of cyclopentane has been investigated in a diaphragmless shock tube with laser schlieren densitometry at nominal post-shock pressures, P_2 , of 35, 70, 150, and 300 Torr and temperatures, T_2 , of 1472-2074 K. These are the first experimental data reported in the high temperature fall-off regime for cyclopentane. The experimental density gradients were simulated using a chemical-kinetic model with good agreement between simulations and experiments. Rate coefficients for dissociation of cyclopentane were obtained and mechanistic details were elucidated. An RRKM model was developed to best fit the experimental results, and the rate coefficients calculated are: $k_{I(35\text{Torr})} = (7.93 \pm 3.96) \times 10^{84} \text{ T}^{-19.815} \exp(-64366/\text{T}) \text{ s}^{-1}$, $k_{I(70\text{Torr})} = (4.79 \pm 2.39) \times 10^{77} \text{ T}^{-17.705} \exp(-62316/\text{T}) \text{ s}^{-1}$, $k_{I(150\text{Torr})} = (2.42 \pm 1.21) \times 10^{69} \text{ T}^{-15.295} \exp(-59862/\text{T}) \text{ s}^{-1}$, $k_{I(300\text{Torr})} = (4.66 \pm 2.33) \times 10^{61} \text{ T}^{-13.065} \exp(-57493/\text{T}) \text{ s}^{-1}$, and $k_{I\infty} = (1.69 \pm 0.85) \times 10^{16} \text{ T}^{-0.005} \exp(-42983/\text{T})$. Results show that cyclopentane dissociation is similar to that of cyclohexane, and involves formation of a biradical intermediate. The high-pressure limit rates for cyclopentane dissociation are also compared with previous results in the literature and show good agreement with a study by Tsang [Int. J. Chem. Kinet. 10 (1978) 599-617].

Keywords: Cycloalkanes, Cyclopentane, Diaphragmless shock tube, Hydrocarbon pyrolysis

Introduction

Cycloalkanes are an important class of molecules observed in many combustion environments and can account for up to 40% of conventional liquid fuels [1–6]. Furthermore, liquid fuels derived from oil sands and shale form an increasing fraction of supplies and contain a higher proportion of cycloalkanes compared to well-oil [7,8]. At high temperatures, pyrolysis of these cyclic species significantly contributes to establishing the radical pool [9] prior to ignition. Furthermore, the decomposition products of cycloalkanes are precursors to polycyclic aromatic pollutants and soot [10]. Consequently, accurate mechanistic and kinetic data that describe the reactions of these compounds are

important for modeling fuel systems to predict ignition properties, reactivity of fuel mixtures, product distributions, and pollutant formation.

The mechanism by which saturated cyclic compounds dissociate is strongly dependent upon the constituent atoms of the ring. For example, the product of cyclohexane pyrolysis is 1-hexene via ring opening and isomerization, possibly through a biradical intermediate [9,11–15]. On the other hand, 1,4-dioxane produces two different linear ethers (ethylene-glycol-vinyl-ether and 2-ethoxyacetaldehyde) via concerted ring opening and hydrogen transfer [16], whereas 1,3,5-trioxane undergoes a concerted dissociation to form three formaldehyde molecules [17–20]. In this experimental study, the effect of reducing a cyclic, saturated hydrocarbon ring from 6 to 5 carbon atoms is examined.

Cyclopentane dissociation has been examined previously in shock tubes under conditions close to or at the high-pressure limit (HPL). Tsang [21] used the comparative rate shock tube method from 1000-1200 K and 2-8 bar with gas chromatography and flame ionization detection to identify products. Tsang concluded that cyclopentane decomposition proceeds initially via ring opening to form a linear biradical that primarily isomerizes to 1-pentene (reaction 1, Table 1) but that a secondary channel, dissociation to cyclopropane and ethylene, also existed. Kalra et al. [22] also used the comparative rate shock tube method but with a different reference reaction from Tsang with a temperature range of 1185-1257 K and similar pressures. The rate coefficients obtained by Kalra et al. are a factor of 3 to 4 higher than those of Tsang, but their activation energy is similar to Tsang's. Kalra et al. argued that this difference could be attributed to the temperatures reported by Tsang being too high by 40 K. Brown et al. [12] also investigated cyclopentane pyrolysis from 1071-1221 K by very low-pressure pyrolysis using mass spectrometry to detect products. By application of Rice-Ramsperger-Kassel-Marcus (RRKM) theory, Brown et al. found good agreement with the previous studies, although their rate coefficients are closer to those of Kalra et al. than Tsang. The dissociation of cyclopentane has also been studied theoretically by Sirjean et al. [13] using quantum chemical calculations to derive rate

coefficients via transition state theory from 600-2000 K. Although the literature k_1 differ by up to a factor of 4, the reported activation energies are consistently around 85 kcal/mol.

The k_1 from Tsang, Kalra et al., and Brown et al. were measured for $T < 1300$ K and are at or near the HPL. Here, experimental and kinetic-modeling studies of the dissociation of cyclopentane in a diaphragmless shock tube (DFST) using laser schlieren densitometry (LS) from 1472-2074 K and 35-300 Torr are presented along with results from an RRKM model for the initial dissociation step. These experiments extend to higher temperatures and lower pressures compared to previous experiments and explore the high-temperature fall-off behavior of cyclopentane pyrolysis, allowing pressure-dependent rate coefficients to be derived. This work is similar to the shock tube/LS investigation of cyclohexane decomposition by Kiefer et al. [9], and allows the effect of reducing ring size to be assessed which should be useful for deriving rate rules for modeling cycloalkanes. It has been suggested that both cyclohexane [9,11–13] and cyclopentane [12,13,21] dissociate via a biradical intermediate, and comparisons between the present work and cyclohexane are made.

Experimental

For the DFST/LS experiments on cyclopentane pyrolysis mixtures of 0.3%, 0.5%, 1%, 2%, 4%, and 6% cyclopentane (Aldrich, 98% purity) in krypton (AirGas, 99.999%) were prepared manometrically in a 50 L evacuated glass mixing vessel. Prior to use, cyclopentane was degassed by multiple freeze-pump-thaw cycles with liquid nitrogen. The DFST [23] and LS technique [24,25] are described in detail elsewhere. Briefly, the driver and driven sections of the DFST are initially isolated by an aluminum plate fitted with a circumferential O-ring that comprises a bellows-actuated, fast-acting valve. The driver and driven sections are respectively filled to pressure P_4 with helium and pressure P_1 with the cyclopentane/krypton mixture. The shock tube is then fired by rapidly opening the fast-acting valve, releasing the high-pressure helium and resulting in formation of a shock wave. A series of five pressure transducers centered around the LS detection window are used to measure the time intervals for

the incident shock wave to pass between successive transducers and thusly derive incident shock wave velocities. The shock velocities along with loading conditions are used to calculate post-shock temperatures and pressures, assuming frozen conditions. The uncertainty in the measured velocities is estimated as 0.2%, which corresponds to an uncertainty in the calculated shock temperatures of approximately 0.5% or 7-10 K.

LS experiments are performed behind the incident shock wave and measure the deflection of a narrow laser beam, which is directed across the shock tube perpendicular to the direction of propagation of the shock wave. The laser beam is deflected first by interaction with the shock front and then by axial density gradients ($d\rho/dx$) in the shock-heated gases resulting from chemical reactions. The measured deflection of the laser beam, θ (Fig. 1, insets), is proportional to the magnitude of the density gradient through Eqn. 1.

$$\theta = \frac{3}{2} K_L W \frac{d\rho}{dx}, \quad (1)$$

where K_L is the mixture molar refractivity and W is the shock tube width. The density gradient (Fig. 1, main panels) is related to the rates of reaction and enthalpies of reaction (ΔH_r) summed over all reactions, j , taking place in the shock-heated mixture, Eqn. 2.

$$\frac{d\rho}{dx} \propto \sum_j r_j (\Delta H_{r,j} - C_p T \Delta N_j), \quad (2)$$

where C_p is the constant pressure heat capacity of the mixture, T is the temperature, and ΔN is the change in mole number.

Fig. 1. Representative semi-log plots of absolute density gradients calculated from LS experiments. The inset of each panel is the raw signal from the LS measurements, with the inset of panel a) showing an expanded x-axis and the inset of panel b) showing an expanded y-axis. Symbols in the main panels are data points from experimental density gradients, with open circles representing positive points, and filled circles representing negative points. Solid lines represent simulations using the mechanism shown in Table S2 of the supplemental information. In panel a), the dashed line is $k_1 \times 1.5$ and the dash-dotted line is $k_1 / 1.5$. The arrow in the inset in panel a) shows the approximate location of t_0 . In panel b), the dashed line represents results from a simulation treating cyclopentane dissociation to ethyl and allyl radicals as a single step, $cC_5H_{10} = C_2H_5 + C_3H_5$, see text for discussion.

At the start of reaction, time t_0 , the only reaction is pyrolysis of cyclopentane, whereas at longer times, the observed density gradients are increasingly influenced by secondary chemistry. For the majority of the experiments reported here, measurements were taken with a helium-neon (HeNe) laser (Spectra Physics Model 120, 632.8 nm, 6 mW, beam diameter = 0.8 mm). More recently, a new optical set up has

been employed consisting of a fiber-coupled Fabry-Perot laser (Thorlabs S1FC637, 637 nm, 8 mW) attached to a single-mode fiber optic, which is terminated with a gradient of refractive index lens. This produces a narrower beam than the HeNe, allowing $\sim 0.2 \mu\text{s}$ more chemical signal to be measured close to t_0 . A new configuration of the shock tube driver section has also recently been implemented [26] and was used to obtain the 1%-concentration dataset. The molar refractivity of Kr is $6.367 \text{ cm}^3 \text{ mol}^{-1}$ [27], and that of cyclopentane is $22.89 \text{ cm}^3 \text{ mol}^{-1}$, which was calculated from its refractive index (1.405) and molar density ($0.01071 \text{ mol mL}^{-1}$) [28]. It is assumed that the molar refractivity does not change over the observation time, which is a good approximation for low concentration mixtures such as these. For example, given an experiment with relatively high concentration (2%), high post-shock pressure, P_2 (300 Torr), and high post-shock temperature, T_2 (1984 K), the mixture molar refractivity would only change by 3% after $3 \mu\text{s}$ and $<10\%$ after $10 \mu\text{s}$, which even for this extreme case results in insignificant changes to the calculated density gradient. The rate coefficients for dissociation of cyclopentane are obtained from (dp/dx) at t_0 and simulation of the early density gradient profiles.

Results and discussion

A total of 113 experiments were performed over nominal post-shock pressures, P_2 , of 35, 70, 150, and 300 Torr and a temperature range of 1472 – 2074 K (see Table S1, supplementary information for all experimental conditions). Example LS signals are shown as insets in Fig. 1, and the signal at $t < 8 \mu\text{s}$ is used to establish a baseline for each experiment. The valley and large peak at around $10 \mu\text{s}$ is due to the shock front interacting with the laser beam. This large peak obscures the start of chemical reaction for about $1 \mu\text{s}$, while the signals at later times are from chemical reaction. Time t_0 is located with an established method [24] to an accuracy of $0.1\text{--}0.2 \mu\text{s}$. The main panels in Fig. 1 show semi-log plots of the absolute density gradients calculated from the raw LS signals. The first few rapidly falling points result from the tail end of the shock wave passing through the laser beam. The density gradients remain

positive over the observation time, indicating that endothermic reactions are most prominent throughout the measurements, but steadily decrease as cyclopentane is consumed and temperature decreases.

Table 1.

Key reactions and Arrhenius parameters for the pyrolysis of cyclopentane^a

#	Reaction	$\log A^b$	n^b	E_a/R^b	$\Delta H_{r,298\text{ K}}^b$	Ref
1	c-C ₅ H ₁₀ = 1-C ₅ H ₁₀				13.3	pw ^c
	HPL	16.228	-0.005	42893		
	300 Torr	61.668	-13.065	57493		
	150 Torr	69.384	-15.295	59862		
	70 Torr	77.680	-17.705	62316		
	35 Torr	84.899	-19.815	64366		
2	1-C ₅ H ₁₀ = C ₂ H ₅ + C ₃ H ₅				72.8	d
	300 Torr	10.960	0	18238		
	150 Torr	10.760	0	18238		
	70 Torr	10.560	0	18238		
	35 Torr	10.360	0	18238		
3	c-C ₅ H ₁₀ = C ₃ H ₆ + C ₂ H ₄	42.350	-9.03	37047	35.8	[21]
6	C ₃ H ₅ = aC ₃ H ₄ + H	82.002	-20.07	47652	58.6	[29] ^e
7	C ₃ H ₅ + H = aC ₃ H ₄ + H ₂	4.3167	2.74	1810	-45.6	e,f
8	C ₃ H ₅ + H = C ₃ H ₆	44.306	-9.24	6104	-86.4	[30] ^e
13	C ₂ H ₄ + H = C ₂ H ₅	41.150	-8.79	5817	-36.0	[31]
39	c-C ₅ H ₁₀ + H = c-C ₅ H ₉ + H ₂	8.3522	2.00	2516	-7.1	[14]

^a Full model, including all 53 reactions, is available in Table S2, supplemental information

^b Units in: cm³, s⁻¹, and kcal. $k = AT^n \exp(-E_a/RT)$.

^c Present work. Uncertainty in k is estimated as $\pm 50\%$

^d Unpublished work, see text

^e rate coefficients were adjusted by up to a factor of 2

^f S. J. Klippenstein, personal communication, 2015

Also shown in Fig. 1 are simulation results calculated using an in-house kinetic modeling code based on the methodology of Gardiner et al. [32] and a chemical kinetic model. The most important reactions for simulating the density gradient profiles are shown in Table 1. The full mechanism consists of 29 species and 53 reactions and is available in Table S2 of the supplementary information. All reactions are treated as reversible, where reverse rate coefficients are calculated via the equilibrium constant for the reaction. Thermodynamic properties were taken from Goos et al. [33]. Experimental and simulated density gradients are most sensitive to reactions that are fast and/or have a large absolute enthalpy of reaction. Throughout the modelling effort, the majority of the rate coefficients were fixed at their literature values, while a small number were varied iteratively for each experiment to visually

obtain the best fit between simulation and experiment. In particular, reactions 6, 7, and 8 were adjusted within a factor of 2 of their literature values, as indicated in Table 1 and discussed later. The early gradient, at times shorter than 2 μ s, is sensitive primarily to k_1 . At longer times, the simulations become sensitive to the other reactions noted in Table 1, which are discussed later.

At time t_0 , the only reactions taking place are unimolecular reactions of cyclopentane, primarily Reaction 1, which is only mildly endothermic (13.3 kcal/mol), resulting in a positive, but relatively small density gradient. The simulations then show a rapid increase at very early times ($< 0.5 \mu$ s) due to the fast and strongly endothermic dissociation of 1-pentene via Reaction 2 (72.8 kcal/mol). This initial rise is obscured by the interaction of the shock front with the laser beam in the measured profiles. Even though Reaction 1 produces relatively little density gradient on its own, the simulations are sensitive to k_1 because Reaction 1 initiates Reaction 2. As shown in Fig. 1a, increasing k_1 causes the simulated density gradient at early times to increase and miss the first few experimental points, but at later times, the simulated density gradient is lower than the experiment as exothermic secondary reactions (e.g., Reaction 8) are promoted by increased production of allyl radicals and hydrogen atoms. Minor adjustments to k_1 were made in an iterative fashion to best fit the experimental data, and the rate of dissociation of cyclopentane is obtained from the initial density gradient $(dp/dx)_0$ by extrapolating the simulations back to t_0 . Arrhenius parameters were then obtained by a least-squares fit, which resulted in temperature-dependent expressions for k_1 for each nominal P_2 within 30% of the value of any individual experiment. Over the range of this work $k_2 = 2.0 \times 10^5$ to $9.4 \times 10^6 \text{ s}^{-1}$ and therefore the simulations are largely insensitive to the exact value.

As shown in Fig. 1b, even though Reaction 2 is very fast under the experimental conditions, attempts to simulate the measured density gradients with a combined Reaction 1 and Reaction 2 (i.e., $\text{cC}_5\text{H}_{10} = \text{C}_2\text{H}_5 + \text{C}_3\text{H}_5$ and $k = k_{\text{combined}}$) did not result in satisfactory agreement between simulations and experiment. The rate coefficients used for the initial cyclopentane dissociation in the two

simulations shown in Fig. 1b were kept equal, i.e., $k_{\text{combined}} = k_1$, as were rate coefficients for all other reactions. Adjustments to rate coefficients to which the density gradient is sensitive (e.g., Reactions 6, 7, and 8) within typical uncertainty were also unable to bring model results into agreement with experimental results across all experimental conditions.

Dissociation of cyclopentane

The 1,5-pentyl biradical has been suggested as a common intermediate prior to either isomerization to 1-pentene or dissociation to cyclopropane and ethylene [12,13,21] and calculated rate coefficients for both channels are $\sim 10^{10} \text{ s}^{-1}$ for $T > 1400 \text{ K}$ [13]. Consequently, cyclopentane decomposition to 1-pentene is treated as a single step (Reaction 1). Similarly, cyclopropane produced will rapidly isomerize to propene ($k \sim 10^6 \text{ s}^{-1}$ [21]), and therefore Reaction 3 is also written as a single step. The branching fraction $k_3/(k_1+k_3)$ was fixed at 0.1, similar to that measured by Tsang (0.07-0.15) [21]. However, the current simulations are insensitive to k_3 , and therefore, the exact branching fraction cannot be determined.

Fig. 2. Arrhenius plots showing rate coefficients for the ring-opening isomerization of cyclopentane to 1-pentene derived from kinetic simulations of LS experiments (symbols). Also shown are results from RRKM calculations at various pressures (broken lines) and the high-pressure limit (solid line). The

figure is broken into two panels to more clearly show the experimental data and associated RRKM results.

Rate coefficients from the LS experiments for Reaction 1 are shown in Fig. 2 and the values are tabulated with experimental conditions in Table S1. The experimental rate coefficients show a small pressure dependence, which is captured by RRKM calculations, Fig. 2. The RRKM model uses molecular properties for cyclopentane and the transition state to the linear biradical from Sirjean et al. [13] with $\langle \Delta E_{\text{down}} \rangle$ and the critical energy, E_0 , adjusted to best fit the experimental data. This resulted in $E_0 = 80.0$ kcal/mol and $\langle \Delta E_{\text{down}} \rangle = 300$ cm⁻¹. The RRKM results agree with the experimental data within ~30%, except for the lowest temperatures (< 1550 K), which differ by up to a factor of 2.

Fig. 3. Arrhenius plots comparing the present results for k_1 at various pressures with those of Tsang [21], Brown et al. [12], Kalra et al. [22], and Sirjean et al. [13].

Figure 3 shows the present results for k_1 along with the HPL rate coefficients given by Tsang [21], Kalra et al. [22], Brown et al. [12], and Sirjean et al. [13]. The HPL rate coefficients calculated from the current RRKM model are within 10% of the values reported by Tsang, and about a factor of 3 to 4 lower than the results reported by Kalra et al. and Brown et al. The calculated HPL activation energy of 85.2 kcal/mol, Table 1, is in good agreement with the prior values of approximately 85 kcal/mol reported by Tsang, Brown et al., and Kalra et al. The HPL RRKM values reported here are smaller by less than 50% compared to those reported by Sirjean et al. within the temperature range of these experiments, but are larger by approximately a factor of 2 at 1000 K.

Cyclopentane pyrolysis shows similar behavior to that of cyclohexane as reported by Kiefer et al. [9] over similar pressure and temperature ranges. The rate coefficients at the HPL for cyclopentane isomerizing to produce 1-pentene (Reaction 1) reported here are a factor of 5 to 10 lower than rate coefficients for cyclohexane producing 1-hexene reported by Kiefer et al. [9]. This is of similar magnitude to the factor of 3 to 5 difference Sirjean et al. [13] calculated for the same reactions. Cyclohexane also undergoes ring-opening isomerization to form 1-hexene, which in turn dissociates to an allyl radical and an n-propyl radical. Tsang [11], Brown et al. [12] and Sirjean et al. [13] proposed the formation of the 1,6-hexyl biradical intermediate in cyclohexane pyrolysis similar to what has been proposed for cyclopentane forming a 1,5-pentyl biradical. Additionally, both ethyl and n-propyl radicals rapidly dissociate via loss of a hydrogen atom; however, 65-75% of n-propyl also dissociates to produce a methyl radical and ethylene [9].

Secondary reactions

After the initial ring opening, the resulting 1-pentene then rapidly dissociates (Reaction 2) to an allyl radical (C_3H_5) and an ethyl radical (C_2H_5). Rates for Reaction 2 were taken from DFST/LS studies on 1-pentene at similar experimental pressures and $1483\text{ K} < T_2 < 1722\text{ K}$. Rate coefficients for dissociation of 1-pentene from this preliminary study provided satisfactory estimates of k_2 , although as noted earlier the simulations are not very sensitive to k_2 .

Fig. 4. Sensitivity of the model to Reactions 6 and 8. The solid line is the best fit simulation to the data seen in Fig. 1a using rate coefficients from Table 1. The dashed line is a simulation using k_6 from

Fernandes et al. [29]. The dash-dotted line is a simulation using k_6 from Fernandes et al. and k_8 from Ye et al. [30].

The products of 1-pentene dissociation, allyl (C_3H_5) and ethyl (C_2H_5) radicals, along with hydrogen atoms, which are primarily formed by ethyl and allyl dissociation, drive most of the secondary chemistry. Under our experimental conditions, ethyl radicals rapidly dissociate to ethylene and a hydrogen atom (the reverse of Reaction 13). The most prominent reactions of allyl radicals are dissociation (Reaction 6), hydrogen abstraction (Reaction 7), and hydrogen addition (Reaction 8). The rates for Reaction 6, which primarily affect the early portion of the density gradient (1-3 μs), Fig. 4, were taken from Fernandes et al. [29] for a pressure of 0.25 bar and adjusted to within a factor of 2. Simulations using k_6 unadjusted from Fernandes et al. fall significantly below the best-fit simulation, as shown in Fig. 4. Reactions 7 and 8 affect later times ($> 4 \mu s$) more strongly compared to Reaction 6 because these reactions become more prominent when a larger concentration of both allyl radicals and hydrogen atoms is present. Rates for Reaction 7 were taken from master-equation calculations for pressures similar to the experiments reported here (S. J. Klippenstein, personal communication, 2015), and the rates for Reaction 8 were taken from Ye et al. [30] for 0.1 bar. Both k_7 and k_8 were lowered by at most a factor of 2 in each simulation to achieve the best fit to the measured data. Using the unadjusted Ye et al. value for k_8 yields similar results to k_6 – simulations fall below the best-fit values. Fig. 4 also shows a model simulation using literature values for both k_6 and k_8 . The adjustments necessary to achieve the best fit to the measured data were evaluated on an experiment-by-experiment basis, and display no discernable pressure dependence, indicating that the pressure dependences in these secondary reactions are too small to be observed by these experiments.

Cyclopentane also undergoes hydrogen abstraction by hydrogen atoms to form a cyclopentyl radical (Reaction 39). Because a significant concentration of hydrogen atoms is formed at early reaction times, the simulations are sensitive to k_{39} , the values for which were taken from Sirjean et al. [14]. The

resulting cyclopentyl radicals rapidly dissociate to primarily form ethylene and an allyl radical [34]. The overall process ($\text{c-C}_5\text{H}_{10} + \text{H} = \text{C}_2\text{H}_4 + \text{C}_3\text{H}_5 + \text{H}_2$) acts to effectively remove hydrogen atoms from the system both because H_2 is formed and because an ethyl radical is prevented from being formed through 1-pentene dissociation.

Propargyl radicals (C_3H_3) are also potentially important to this system and are formed via allene dissociation (Reaction 43: $\text{aC}_3\text{H}_4 = \text{C}_3\text{H}_3 + \text{H}$). Propargyl is a known source of benzene and other aromatics (see, for example, Tang et al. [35]). Although propargyl recombination can form any of several aromatic and non-aromatic C_6H_6 isomers, the model presented here only includes the production of benzene. Benzene formation is the most exothermic reaction of propargyl recombination (-146.4 kcal/mol), and therefore represents an upper limit for the influence propargyl-recombination chemistry has on the density gradients. The model shows only minor sensitivity to this reaction (Reaction 53), and therefore it is concluded that this reaction is not important at the conditions or on the timescale of these experiments.

Summary

The rate of cyclopentane pyrolysis has been studied in a diaphragmless shock tube using laser schlieren densitometry, and a chemical kinetic model was developed to simulate the results. The experimental conditions extend to higher temperatures and lower pressures than previous experimental studies and allowed accurate, pressure-dependent rate coefficients to be calculated. An RRKM model was developed to fit the experimental data at different pressures and the rate constant for ring-opening isomerization (k_1) agrees with the results of Sirjean et al. [13] to within 50% at the HPL and temperature range of these experiments. The calculated activation energy for ring-opening isomerization is similar to that reported by Tsang [21], Kalra et al. [22], Brown et al. [12], and Sirjean et al. [13]. Cyclopentane exhibits a pyrolysis mechanism similar to cyclohexane, first undergoing ring-opening isomerization, possibly via a biradical intermediate to primarily form 1-pentene, before dissociation to an allyl radical

and an ethyl radical. The rate expressions reported here in conjunction with previous investigations of cyclohexane should be useful for deriving rate rules for modeling cycloalkanes in combustion systems.

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Appendix A: Supplementary material

Tables with the full mechanism and Arrhenius parameters and experimental conditions can be found in the supplementary material.

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Figure captions:

Fig. 1. Representative semi-log plots of absolute density gradients calculated from LS experiments. The inset of each panel is the raw signal from the LS measurements, with the inset of panel a) showing an expanded x-axis and the inset of panel b) showing an expanded y-axis. Symbols in the main panels are data points from experimental density gradients, with open circles representing positive points, and filled circles representing negative points. Solid lines represent simulations using the mechanism shown in Table S2 of the supplemental information. In panel a), the dashed line is $k_1 \times 1.5$ and the dash-dotted line is $k_1 / 1.5$. The arrow in the inset in panel a) shows the approximate location of t_0 . In panel b), the dashed line represents results from a simulation treating cyclopentane dissociation to ethyl and allyl radicals as a single step, $\text{cC}_5\text{H}_{10} = \text{C}_2\text{H}_5 + \text{C}_3\text{H}_5$, see text for discussion.

Fig. 2. Arrhenius plots showing rate coefficients for the ring-opening isomerization of cyclopentane to 1-pentene derived from kinetic model fits to LS experiments (symbols). Also shown are results from RRKM calculations at various pressures (broken lines) and the high-pressure limit (solid line). The figure is broken into two panels to more clearly show the experimental data and associated RRKM results.

Fig. 3. Arrhenius plots comparing the present results with those of Tsang [17], Brown et al. [8], Kalra et al. [18], and Sirjean et al. [9].

Fig. 4. Sensitivity of the model to Reactions 6 and 8. The solid line is the best-fit simulation to the data seen in Fig. 1a using rate coefficients from Table 1. The dashed line is a simulation using k_6 from Fernandes et al. [25]. The dash-dotted line is a simulation using k_6 from Fernandes et al. and k_8 from Ye et al. [26].