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A shock tube laser schlieren study of cyclopentane pyrolysis

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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: $k_{1(35\,\mathrm{Torr})} = (7.93 \pm 3.96) \times 10^{84}\ T^{-19.815}\ \exp(-64366/T)\ \mathrm{s}^{-1}$, $k_{1(70\,\mathrm{Torr})} = (4.79 \pm 2.39) \times 10^{77}\ T^{-17.705}\ \exp(-62316/T)\ \mathrm{s}^{-1}$, $k_{1(150\,\mathrm{Torr})} = (2.42 \pm 1.21) \times 10^{69}\ T^{-15.295}\ \exp(-59862/T)\ \mathrm{s}^{-1}$, $k_{1(300\,\mathrm{Torr})} = (4.66 \pm 2.33) \times 10^{61}\ T^{-13.065}\ \exp(-57493/T)\ \mathrm{s}^{-1}$, and $k_{1\infty} = (1.69 \pm 0.85) \times 10^{16}\ T^{-0.005}\ \exp(-42983/T)$. 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 (1978) [21].

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

1. 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

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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 to 1200 K and 2 to 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 3–4 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 to 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 to 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 to 2074 K and 35 to 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

Table 1
Key reactions and Arrhenius parameters for the pyrolysis of cyclopentane[a].

#	Reaction	log A[b]	n[b]	E_a/R[b]	$\Delta H_{r,298\,K}$[b]	Ref
1	$c\text{-}C_5H_{10} = 1{-}C_5H_{10}$				13.3	pw[c]
	HPL	16.228	−0.005	42,893		
	300 Torr	61.668	−13.065	57,493		
	150 Torr	69.384	−15.295	59,862		
	70 Torr	77.680	−17.705	62,316		
	35 Torr	84.899	−19.815	64,366		
2	$1\text{-}C_5H_{10} = C_2H_5 + C_3H_5$				72.8	*d*
	300 Torr	10.960	0	18,238		
	150 Torr	10.760	0	18,238		
	70 Torr	10.560	0	18,238		
	35 Torr	10.360	0	18,238		
3	$cC_5H_{10} = C_3H_6 + C_2H_4$	42.350	−9.03	37,047	35.8	[21]
6	$C_3H_5 = aC_3H_4 + H$	82.002	−20.07	47,652	58.6	[29][e]
7	$C_3H_5 + H = aC_3H_4 + H_2$	4.3167	2.74	1810	−45.6	*e,f*
8	$C_3H_5 + H = C_3H_6$	44.306	−9.24	6104	−86.4	[30][e]
13	$C_2H_4 + H = C_2H_5$	41.150	−8.79	5817	−36.0	[31]
39	$c\text{-}C_5H_{10} + H = c\text{-}C_5H_9 + H_2$	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: cm^3, s^{-1}, and kcal. $k = AT^n exp(-E_a/RT)$.
[c] Present work. Uncertainty in k is estimated as ± 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.