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## Kinetics of H Atom Addition to Cyclopentene

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**Abstract:** To provide benchmark information needed to develop kinetic models of the combustion and pyrolysis of hydrocarbon ring structures, we have used the single pulse shock tube technique to study the kinetics of H atom addition to cyclopentene at 863 K to 1167 K and pressures of 160 kPa to 370 kPa. Addition of H to the pi bond leads to the cyclopentyl radical, which rapidly decomposes to ethene and allyl radical. Rate constants for the overall process were determined relative to a reference reaction via post-shock GC/FID/MS monitoring of products. A Transition-State-Theory/Rice-Ramsberger-Kassel-Marcus (TST/RRKM) model has been applied in conjunction with evaluated literature data to convert the primary measurements to a high pressure limiting rate expression for H addition. Results are compared with related systems. Near 1000 K, our data require a minimum value of 1.5 for branching between beta C-C and C-H bond scission in cyclopentyl radicals to maintain established trends in H addition rates. This minimum is consistent with a branching value of about 3 that we determined in previous experiments, but conflicts with much smaller values derived by current computations and those used in recent kinetics models to describe jet-stirred reactor studies of cyclopentane combustion.

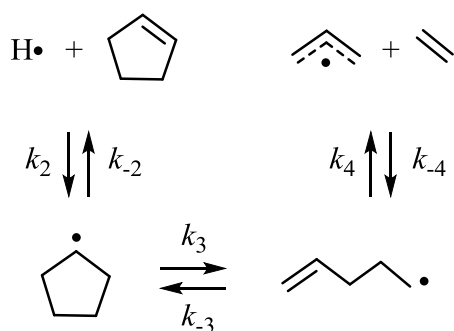
**Keywords:** *Kinetics, Fuels, Cyclopentyl, Shock Tube, RRKM*

### 1. Introduction

Cyclopentene (CPE) is a combustion intermediate and component of some fuels. It is the smallest hydrocarbon having an unsaturated C5 ring and is a prototypical species useful for predicting the behavior of larger analogs. Such ring structures may be present in liquid fuels or may arise from the short chain radicals and olefinic species formed during the breakup of larger fuels. The reaction of these species with small radicals leads to polycyclic aromatic hydrocarbons (PAH's), finally terminating with particulate soot,[1] which is an environmental and regulatory concern. Our interest is related to the development of reliable kinetic models for the combustion of cyclic fuels and their conversion to PAH. Benchmark information on the base ring structure is expected to provide useful information needed to reliably extend the models to larger systems

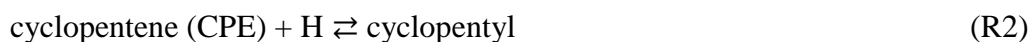
We report herein the use the shock tube technique to determine rate constants for the addition of H atoms to cyclopentene at temperatures near 1000 K. We also use a TST/RRKM model to explore the relationship of this process to the subsequent decomposition of the cyclopentyl adduct radical. Addition of H to cyclopentene forms the cyclopentyl radical, which at higher temperatures undergoes rapid ring opening and decomposition to ethene and allyl radical.[2-5] Ring opening competes with the re-ejection of a hydrogen atom, the kinetics of which is related to H addition through detailed balance. The overall decomposition is:





**Scheme 1:** Decomposition of cyclopentene (CPE) induced by addition of H atoms.

As depicted in Scheme 1, The process consists of three elementary reactions, R2 to R4:



Although the mechanism is established, there is conflicting information about the various rate constants, and it is the balance of the various elementary reactions that determines the overall behavior under conditions of interest.

In experimental work reported in 2011 we measured the branching between cyclopentene and ethene products in the decomposition of cyclopentyl radical under conditions similar to the present experiments and developed a TST/RRKM model of R2 to R4.[2] Our measured ratio for CC/CH beta scission in cyclopentyl ( $k_3/k_{-2}$ ) was about an order of magnitude larger than values derived by computation.[5] In the intervening years a number of relevant studies have been reported. Pertinent to  $k_{-3}$  (Scheme 1), Wang *et al.*[6] in 2015 derived structure activity rate estimation rules for ring closure in C<sub>4</sub> to C<sub>8</sub> alkenyl radicals. Herbinet *et al.*[1] studied and modeled cyclopentene pyrolysis and formation of the first aromatic ring in a jet-stirred reactor (JSR) in 2016. Finally, in 2017 Al Rashidi *et al.*[7] reported a study of cyclopentane combustion in a JSR and developed a detailed kinetic model to describe the results. They found unusual inhibition behavior and their model showed that the relative and absolute rate constants for cyclopentyl radical decomposition were critical parameters. They were unable to model their results using the rate constants and  $k_3/k_{-2}$  branching ratios we reported in 2011.

In the present work, we use thermal precursors to create H atoms in the presence of a large excess of cyclopentene and an additional reference compound. The stable ethene product of R1 is quantitated in post-shock GC analyses and compared with the amount of product formed by attack of H on the reference species This directly yields relative rate constants, which are then converted to absolute values of R1 based on the reference rate. We combine our data with computations and various literature data to create a detailed kinetic model that relates the results to the elementary reactions of Scheme 1. Our data and analysis lead to reliable high pressure rate expression for  $k_2$  and an independent method of estimating  $k_3/k_{-2}$ .

## 2. Methods / Experimental

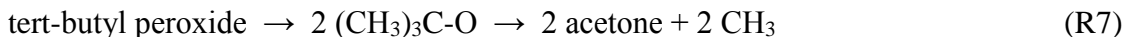
Experiments are carried out in a heated single pulse shock tube having an  $\approx 500 \mu\text{s}$  reaction time and described in earlier publications.[8] In the current studies, reactants are highly diluted in

a bath gas of argon and we use small quantities of a precursor [ $\approx 50 \mu\text{L/L}$  (ppm)] to create a limited number of H atoms in the presence of much larger quantities ( $\approx 10,000 \mu\text{L/L}$ ) of cyclopentene and 1,3,5-trimethylbenzene (135TMB). The latter compound serves as both a rate reference for H atom reactions and a radical scavenger. A Hewlett Packard 6890 N gas chromatograph equipped with FID and MS detection is used to measure the post-shock products. Including systematic errors, analytical uncertainties ( $2\sigma$ ) for the main products are estimated as 6 %.

*Generation of H atoms.* We have used three different methods to thermally produce H atoms. On the  $\approx 500 \mu\text{s}$  time scale of our experiments, thermolysis of hexamethylethane (HME) is an effective source of H at temperatures  $> 1000 \text{ K}$ :



To probe lower temperatures, a few experiments were conducted with mixtures containing small amounts ( $\approx 25 \mu\text{L/L}$ ) of tert-butyl peroxide (tBPO) and a large amount of  $\text{H}_2$  ( $\approx 20 \%$ ), which leads to H atoms via the following sequence:



Although useful as a confirmatory technique, we found this method to be of limited value due to the loss of methyl radicals to side reactions. The decomposition of 2-iodopropane proved to be a more effective source of H atoms at temperatures  $< 1000 \text{ K}$ . 2-Iodopropane undergoes both molecular elimination of HI and fission of the weak C-I bond. The latter process generates an isopropyl radical that rapidly ejects H:



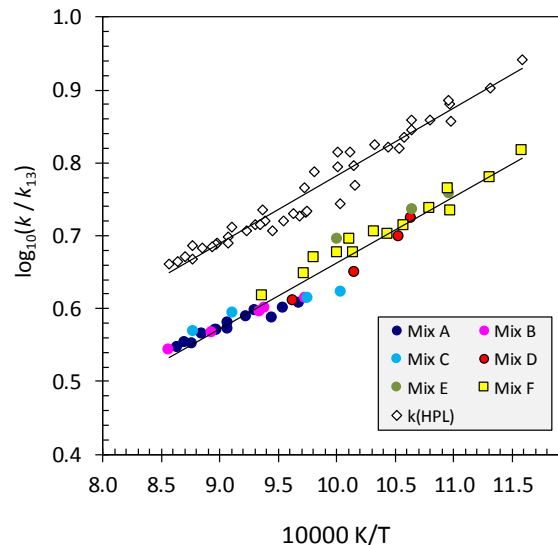
We determine rate constants for the reaction of H with CPE relative to known values for the reaction of H with 135TMB. Attack of H on 135TMB leads either to  $\text{H}_2$  and dimethylbenzyl radical (DMB) or displacement of methyl to give *m*-xylene:



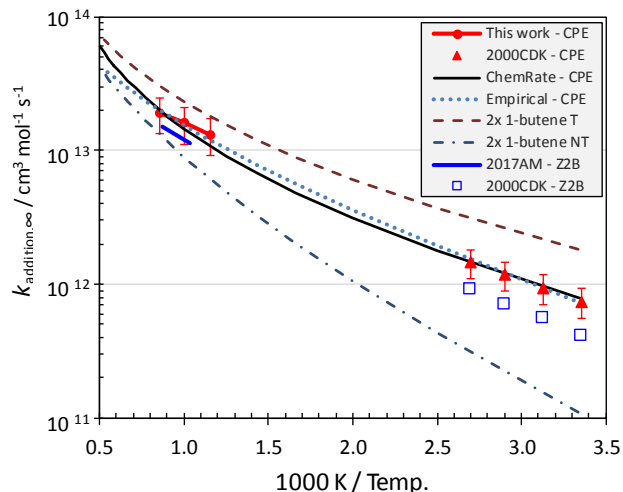
Near 1000 K the branching is about 2:1 in favor of abstraction.[9] DMB does not readily propagate radical chains and inhibits secondary chemistry through recombination reactions. Formation of *m*-xylene through R13 is a highly specific rate reference for reactions of H atoms. For R13 we use the rate parameters of Tsang et al.[9],  $k(\text{H} + 135\text{TMB} \rightarrow m\text{-xylene} + \text{CH}_3) = 6.7 \times 10^{13} \exp(-3255/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . At our temperatures the uncertainty in  $k_{13}$  is about a factor of 1.5.[9] The existing database of rate constants measured relative to R13 provides valuable comparisons and a consistent scaling of absolute values.

### 3. Results and Discussion

Matheu et al.[10] used a mechanism generating computercode to identify 70 possible product channels in the H + cyclopentene addition reaction, but concluded that the reactions of Scheme 1 are the only important unimolecular processes. Our experimental product data support this



**Figure 1.** Experimental rate constant ratios for  $k_1/k_{13}$  (filled markers) and the corresponding high pressure limit values for  $k_{2(\infty)}/k_{13}$  (unfilled markers) derived after applying an experimentally based correction for branching in the decomposition of the cyclopentyl radical (see text).



**Figure 2.** High pressure rate constants for addition of H to CPE and selected alkenes.; Z2B = (*Z*)-2-butene; T = terminal site; NT = nonterminal site. Dotted and solid lines indicate respective empirical and TST fits to the CPE data. Indicated uncertainties are  $2\sigma$ . Data for 1-butene are multiplied by 2 to normalize the number of sites relative to CPE. Data sources: CPE[11]; 1-butene[8]; Z2B[11, 12].

conclusion. Thus, ethene formation is directly related to the overall reaction  $\text{CPE} + \text{H} \rightarrow \text{cyclopentyl} \rightarrow \text{ethene} + \text{allyl}$  (R1). The rate of this reaction relative to R13 is given by the molar yields of ethene and *m*-xylene normalized by the ratio of the reactants,  $k_1/k_{13} = [\text{ethene}][135\text{TMB}]/[m\text{-xylene}][\text{CPE}]$ . These data are plotted in Figure 1 and give:

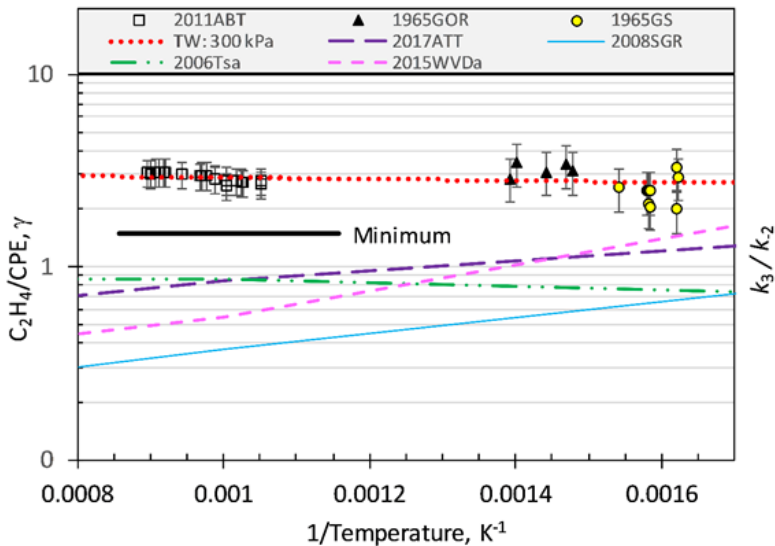
$$\frac{k_1}{k_{13}} = 10^{-0.196 \pm 0.062} \exp[(1995 \pm 60) \text{ K}/T]; 863 \text{ K to } 1167 \text{ K}$$

The given uncertainties are  $2\sigma$  and represent precision only. Including systematic errors, the overall uncertainty ( $2\sigma$ ) in the relative rate is estimated as about  $\pm 15\%$ . Using  $k_{13}$  we derive:

$$k_1 = 4.27 \times 10^{13} \exp(-1260 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}; 863 \text{ K to } 1167 \text{ K}$$

The uncertainty ( $2\sigma$ ) in the absolute rate constant is about a factor of 1.5 and is due mainly to the uncertainty in the rate of the reference reaction. Because addition of H to cyclopentene, R2, is partially reversible,  $k_1$  represents the minimum possible value of  $k_2$ . Assuming all H additions yield either ethene or cyclopentene as a stable olefin, then  $k_{2(\infty)} = k_1(\gamma+1)/\gamma$ , where  $\gamma$  is the molar product ratio,  $[\text{ethene}]/[\text{CPE}]$ , in the decomposition of the cyclopentyl radicals formed by R2.

As reported in 2011,[9] we have previously measured values of  $\gamma$  by creating cyclopentyl radicals under dilute conditions and directly observing the ethene/CPE product ratio. G3MP2B3 computations were used to compute energies and other properties and an RRKM master equation analysis of the system depicted in Scheme 1 was carried out with ChemRate software[13]. The initial theoretical model was minimally tuned to match available data. Presently, we have slightly updated the 2011 model to better match additional literature information and then used it to derive values of  $\gamma$  for the chemically activated cyclopentyl radicals formed in the current experiment. Computed  $\gamma$  values are about 3 and little changed from the thermal values under our conditions. They lead to values of  $k_{2(\infty)}$  that are about 30 % larger than  $k_1$  (Figure 1). For  $k_{2(\infty)}$ , we find:



**Figure 3.** Branching in cyclopentyl decomposition. The symbols and dotted line show ethene/cyclopentene product ratios ( $\gamma$ , left axis) from experiment and our model at 300 kPa, respectively; the other lines are  $k_3/k_{-2}$  values (right axis) at the high pressure limit, which are approximately equivalent. The indicated minimum is that required by our current experiments to maintain consistency in H atom addition rates. Product ratios of 1965GOR[3] 1965GS[4] are plotted only at their higher temperatures where they relate to  $k_3/k_{-2}$ . Values from 1965GS are corrected for cyclopentene formed by disproportionation of cyclopentyl using  $k_{\text{dis}}/k_{\text{rec}} = 1$  as reported in that work. Data sources: TW, this work; 2011ABT[2]; 2006Tsa[14]; 2017ATT[7]; 2015WVDA[6]; 2008SGR[5].

$$k_{2(\infty)} = 5.37 \times 10^{13} \exp(-1213 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}; 863 \text{ K to } 1167 \text{ K}$$

Our TST/RRKM model has been tuned to fit the present data as well as those of Clarke *et al.* at 298 K to 370 K, and results in  $k_{2(\infty)} = 9.09 \times 10^7 T^{1.783} \exp(-324 \text{ K}/T)$  between 298 K and 2000 K. Comparisons with pertinent data are presented in Figure 2. Data near 1000 K are from this laboratory and are all derived relative to  $k_{13}$ . The addition rate of H to cyclopentene lies between those for terminal and nonterminal addition of H to 1-butene and is slightly faster than the analogous reaction with (Z)-2-butene, a noncyclic analog.

We have derived  $k_{2(\infty)}$  using  $\gamma$  values of about 3. At our temperatures, values of  $\gamma$  less than 1.1 would require, on a per site basis, that the high pressure rate constant for H atom addition to cyclopentene exceed that for terminal addition of H to 1-butene. Such a result would be strongly at odds with known trends in rates of H atom addition to olefins. To maintain self-consistency in H atom addition rates, the reasonable lower limit of  $\gamma$  is about 1.5. This derived minimum is consistent with our measured  $\gamma$  values (about 3), but is obtained in an independent manner. It is at odds, however, with  $\gamma$  values derived from computations and used in current kinetics models of cyclopentane combustion, all of which are in the range of 0.3 to 0.8 near 1000 K.

Figure 3 summarizes experimental values of  $\gamma$  and theoretical values for the closely related branching ratio  $k_3/k_{-2}$ . The two are not strictly identical because of the slight reversibility of ring opening (about 5%), but all current models agree that the difference is minimal. Note that extrapolation of the experimental  $\gamma$  values to high pressure limits would slightly increase differences with the  $k_3/k_{-2}$  values. The experimental product ratios exhibit only a weak temperature dependence between 600 K and 1100 K. These values are derived from GC measurements having high precision, so significant errors would have to be systematic and related to the mechanism assumed in the data analyses. Both Gordon[3] and Gunning and Stock[4] conclude that in their

studies cyclopentene is formed at lower temperatures primarily by disproportionation reactions of cyclopentyl. The data from these works plotted in Figure 3 are from their higher temperatures where C-H bond scission is believed to be the dominant source of cyclopentene, conditions where ethene/cyclopentene ratios should be closely related to  $k_3/k_{-2}$ . Notice that contributions from disproportionation would tend to make the derived ratios too small and would further increase the discrepancy with the values from theory or used in the modeling work.

In their experimental and modeling study of cyclopentane combustion in a JSR, Al Rashidi *et al.*[7] showed that the relative and absolute rate constants for cyclopentyl radical decomposition were critical parameters in their detailed kinetic model. They were unable, however, to reproduce the observed reactivity and inhibition behavior without using branching ratios much smaller than we reported in 2011.[2] Nonetheless, the present data and analysis appears to independently confirm the 2011 results. The reasons for this apparent disagreement remain to be explained.

#### 4. Conclusions

Shock tube methods have been used to investigate the addition of H atoms to cyclopentene at temperatures of (863 to 1167) K and pressures of (160 to 370) kPa. Addition of H to the double bond leads to a cyclopentyl radical that rapidly ring opens and decomposes to ethene and allyl radical. We have determined rate constants for the overall process and related these to the high pressure limiting rate constant for H atom addition. The data allow the relative and absolute rates of CC and CH  $\beta$ -scission in cyclopentyl radical to be deduced. Near 1000 K, ratios of CC to CH scission smaller than about 1.5 are shown to result in inconsistencies in known relative rates of H atom addition to olefins. The present data are consistent with branching values near 3 as determined in our previous work, but do not agree with reported much smaller values derived from theoretical studies or those seemingly required in detailed kinetic models of cyclopentane combustion to explain the observed global reactivity behavior.

#### 6. References

- [1] O. Herbinet, A. Rodriguez, B. Husson, F. Battin-Leclerc, Z.D. Wang, Z.J. Cheng, F. Qi, *J. Phys. Chem. A* 120 (2016) 668-682.
- [2] I.A. Awan, D.R. Burgess, Jr., W. Tsang, J.A. Manion, *Proc. Combust. Inst.* 33 (2011) 341-349.
- [3] A.S. Gordon, *Can. J. Chem.* 43 (1965) 570-581.
- [4] H.E. Gunning, R.L. Stock, *Can. J. Chem.-Rev. Can. Chim.* 42 (1964) 357-370.
- [5] B. Sirjean, P.A. Glaude, M.F. Ruiz-Lopez, R. Fournet, *J. Phys. Chem. A* 112 (2008) 11598-11610.
- [6] K. Wang, S.M. Villano, A.M. Dean, *J. Phys. Chem. A* 119 (2015) 7205-7221.
- [7] M.J. Al Rashidi, S. Thion, C. Togbe, G. Dayma, M. Mehl, P. Dagaut, W.J. Pitz, J. Zador, S.M. Sarathy, *Proc. Combust. Inst.* 36 (2017) 469-477.
- [8] J.A. Manion, I.A. Awan, *J. Phys. Chem. A* 119 (2015) 429-441.
- [9] W. Tsang, J.P. Cui, J.A. Walker, *Single Pulse Shock Tube Studies on the Reactions of Hydrogen Atoms with Unsaturated Compounds*, Proceedings of the 17th International Symposium on Shock Waves & Shock Tubes, Bethlehem, PA, AIP Conference Proceedings 208, American Institute of Physics, Melville, NY, 1990, pp. 63 - 73, DOI: 10.1063/1061.39497.
- [10] D.M. Matheu, W.H. Green, J.M. Grenda, *Int. J. Chem. Kinet.* 35 (2003) 95-119.
- [11] J.S. Clarke, N.M. Donahue, J.H. Kroll, H.A. Rypkema, J.G. Anderson, *J. Phys. Chem. A* 104 (2000) 5254-5264.
- [12] I.A. Awan, J.A. Manion, unpublished work, 2018.
- [13] V. Mokrushin, V. Bedanov, W. Tsang, M. Zachariah, V.D. Knyazev, W.S. McGivern, *ChemRate*, National Institute of Standards and Technology, Gaithersburg, Maryland, 1996-2011.
- [14] W. Tsang, *J. Phys. Chem. A* 110 (2006) 8501-8509.