



Shock tube measurements of the rate constant for the reaction cyclohexene \rightarrow ethylene + 1,3-butadiene



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ARTICLE INFO

Article history:

Received 2 April 2013

In final form 26 July 2013

Available online 20 August 2013

ABSTRACT

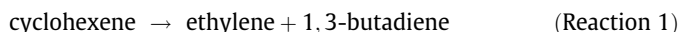
The rate constant for the reaction cyclohexene \rightarrow ethylene + 1,3-butadiene was determined by monitoring the formation of ethylene during the pyrolysis of cyclohexene behind reflected shock waves. Ethylene mole-fraction time-histories were measured using direct laser absorption at 10.532 μm . Experiments were performed between 950–1300 K and 0.8–3.7 atm. Measurements do not indicate any pressure dependence at these conditions. The data are best-fit by an Arrhenius expression $k [\text{s}^{-1}] = 4.84 \times 10^{14} \exp(-31900 [\text{K}]/T)$ with uncertainties of ± 19 –36%, depending on the temperature. This appears to be the most accurate determination to date of the rate constant for cyclohexene decomposition.

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1. Introduction

Shock tubes are a valuable tool used to study high-temperature chemical kinetics. A common experimental technique deployed to measure rates of reaction, especially in single pulse shock tubes, is the comparative rate method [1], where the rate constant of a test reaction is measured relative to that of a reference reaction. If the rate constant for the reference reaction is well-known, the absolute rate constant for the test reaction can be inferred. The reference reaction can also be used as a chemical thermometer to explicitly determine the experimental temperature, which is critical in experiments where the rate constants of the reference and test reactions have different temperature dependences. Both comparative rate and chemical thermometry methods require accurate knowledge of the rate constant for the reference reaction as a function of temperature and pressure.

A common reaction used as reference near 1000 K is the decomposition of cyclohexene via the pathway shown in *Reaction 1*.



The rate constant for *Reaction 1* has been studied extensively using a variety of experimental methods [2–14]. Based on the detected species during the decomposition of cyclohexene, all-but-one of these past studies concluded that *Reaction 1* is the major decomposition pathway at temperatures between 700 and 1200 K. However, a single study [13] measured the rate constant for alternative decomposition pathways and found that decomposition to 1,3-cyclohexadiene and H_2 accounts for approximately 40% of cyclohexene decomposition at temperatures near 500 K. Nonetheless, the scientific community generally agrees that

Reaction 1 is the major cyclohexene decomposition pathway in the temperature range where cyclohexene decomposition is typically used as a reference reaction, between 950 and 1100 K. In this study, the rate constant for *Reaction 1* was determined by observing the rate of formation of ethylene using direct laser absorption during the decomposition of cyclohexene behind reflected shock waves. These appear to be the most accurate measurements of the rate constant for *Reaction 1* thus far at elevated temperatures, and the results are in fair agreement with past studies.

2. Experimental setup

Experiments were performed behind reflected shock waves in the Stanford kinetics shock tube with a 14.13 cm inner diameter. Further details on this facility are provided elsewhere [15,16]. Mixtures were prepared manometrically and were diluted in argon. Direct laser absorption at 3.39 μm was used to confirm that the initial cyclohexene mole fraction inside the shock tube was equal to the manometrically calculated value inside the mixing tank. Details on this diagnostic are described elsewhere [15]. The room temperature absorption cross-section of cyclohexene at 3.39 μm was measured to be 33.9 $\text{m}^2 \text{mol}^{-1}$, in excellent agreement with the value of 33.0 $\text{m}^2 \text{mol}^{-1}$ from the PNNL database [17].

The ethylene mole fraction was measured using direct laser absorption at 10.532 μm generated by a tunable CO_2 gas laser. Further details on the ethylene diagnostic are provided elsewhere [18,19]. In this study, it was necessary to consider absorption of cyclohexene and 1,3-butadiene at 10.532 μm when calculating the mole fraction of ethylene. As explained later in this section, ethylene and butadiene are stable species at the conditions in this study, and their concentrations are equal in these experiments because they are produced in a one-to-one ratio via *Reaction 1*. Furthermore, assuming that *Reaction 1* is the dominant cyclohexene

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decomposition pathway, the mole fraction of cyclohexene is related to that of ethylene by the simple relation:

$$x_{\text{ethylene}} = x_{\text{cyclohexene,initial}} - x_{\text{cyclohexene}}$$

Therefore, since the mole fractions of cyclohexene, butadiene, and ethylene are directly related, the ethylene mole fraction can be explicitly calculated from the measured transmission via the relations:

$$T = \exp(-\alpha)$$

$$x_{\text{eth}} = \frac{\frac{\alpha}{nL} - \sigma_{\text{cyc}} x_{\text{cyc,init}}}{\sigma_{\text{eth}} + \sigma_{\text{but}} - \sigma_{\text{cyc}}}$$

where T is the measured transmission, α is the absorbance, n is the total number density, L is the total pathlength through the shock tube, and x_i and σ_i are the mole fraction and absorption cross-section of the absorbing species, respectively.

The absorption cross-section of ethylene at 10.532 μm was taken from previous work [18], and the absorption cross-section of cyclohexene, butadiene, and 1,3-cyclohexadiene at 10.532 μm were measured behind reflected shock waves in this study. The measured absorption cross-sections exhibited no pressure dependence between 1.5 and 3.8 atm, and the results are summarized in Figure 1. Since the absorption cross-section of cyclohexene is over an order of magnitude lower than that of ethylene and 1,3-butadiene, the above analysis which accounts for the variations in absorbance caused by the reduction in the cyclohexene mole fraction results in only a minor perturbation on the measurement of the ethylene mole fraction. In addition, since the absorption cross-section of 1,3-cyclohexadiene is low compared to that of ethylene and 1,3-butadiene, and since the alternative cyclohexene decomposition pathway to 1,3-cyclohexadiene and H_2 (which does not absorb 10.532 μm light) is at least an order of magnitude slower than the primary decomposition pathway shown in Reaction 1 (see discussion in the Kinetic Modeling Section), decomposition of cyclohexene via this alternative pathway would not perturb the measured ethylene mole fraction by more than 2.5%.

3. Kinetic modeling

Simulations were performed using the CHEMKIN-PRO kinetics solver assuming a constant volume, constant internal energy mod-

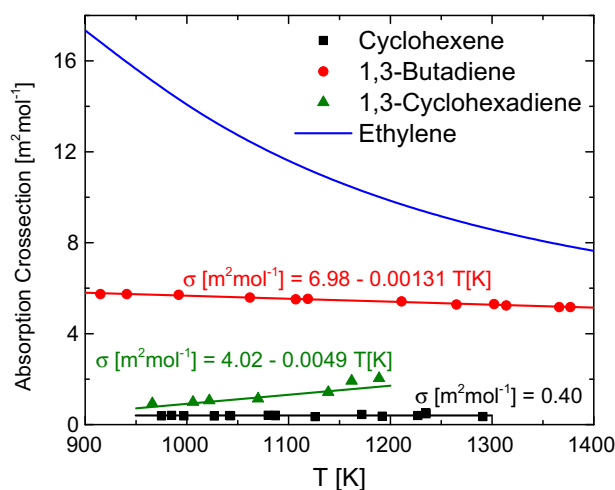


Figure 1. Absorption cross-sections of cyclohexene, 1,3-butadiene, 1,3-cyclohexadiene, and ethylene at 10.532 μm . Cyclohexene, 1,3-butadiene, and 1,3-cyclohexadiene cross-sections measured in this study from 1.5 to 3.8 atm. Ethylene cross-section taken from previous work and plotted for 2 atm [18].

el. A comprehensive cyclohexane mechanism by Silke et al. [20] was used as a basis for secondary reactions that may occur in the shock tube. However, since this mechanism was not validated for cyclohexene decomposition, the rate constants of several potential secondary reactions were added and modified based on the latest values suggested in the literature, as summarized in Table 1. Though the rate constants for H-atom abstraction reactions from cyclohexene by H-radicals were not modified, it was verified that these reactions had reasonable rate estimates in the Silke et al. [20] mechanism. The mechanism also indicates that H-radical generation is negligible at the conditions in this study, because kinetic pathways that lead to H-radicals are at least two orders of magnitude slower compared to decomposition of cyclohexene via Reaction 1. Therefore, since H-radical generating pathways are very slow at the conditions in this study, simulations are not affected by these reaction pathways and high-accuracy rate constant estimates for cyclohexene + H reactions are not necessary.

As expected, rate-of-production analysis indicates that virtually all chemical processes occur via Reaction 1 at the conditions studied. The mechanism also confirms that 1,3-butadiene and ethylene are equimolar at low conversion rates of cyclohexene because their overall unimolecular decomposition rate constants are slower than that of Reaction 1 by a factor of 300 at the conditions in this study. This is explicitly confirmed in past studies by Tsang [3] and Heyne et al. [21], the latter of which indicates that ethylene and 1,3-butadiene are equimolar even at 60% conversion rates of cyclohexene.

Simulations were performed with a rate constant estimate for the reaction cyclohexene \rightarrow 1,3-cyclohexadiene + H_2 nominally equal to zero. Though the rate constant for this reaction was measured previously to be approximately one third of that for Reaction 1 near 500 K [13], several subsequent studies have concluded that this pathway must be negligible at temperatures below 1200 K, based on the observed pyrolysis products of cyclohexene decomposition [3,5–7]. Therefore, past work suggests that this pathway is approximately one to two orders of magnitude slower compared to that of Reaction 1 below 1200 K, though an agreed upon reaction rate constant in the literature does not exist. Brute force analysis using an assumed rate constant for the reaction cyclohexene \rightarrow 1,3-cyclohexadiene + H_2 that is up to 10% of the value for Reaction 1 does not perturb the experimentally inferred rate constant for Reaction 1 by more than 2%. This is expected because the decomposition of cyclohexene via alternative pathways does not significantly perturb the absolute cyclohexene mole fraction at low conversion rates where simulations were fit to experimental data. Therefore, since the rate of ethylene formation via Reaction 1 is proportional to the concentration of cyclohexene, it remains unperturbed by alternative cyclohexene decomposition pathways at low conversion.

At a given post-reflected-shock condition, the rate constant for Reaction 1 was inferred by adjusting its Arrhenius A-factor to achieve a best-fit between simulations and measurements of ethylene formation. Simulations were performed using a temperature-dependent rate constant for the title reaction in order to account for small temperature changes which may occur throughout the measurement time at high post-reflected-shock temperatures, due to the endothermic decomposition of cyclohexene (details are provided in following paragraphs). Data presented in this study are the values of the rate constant for Reaction 1 at the initial post-reflected-shock temperature, calculated using the fitted Arrhenius A-factor and the Arrhenius activation energy from the simulation. As a starting point, data was analyzed using a value of the activation energy for Reaction 1 suggested by Tsang (1973) [4]. Measurements of the rate constant as a function of temperature were then used to calculate a new activation energy, and the above data analysis procedure was repeated. Values of the measured reaction rate constant converged after a single iteration,

Table 1

Rate constant for reactions modified and added to the Silke et al. [20] mechanism. Units: s^{-1} (unimolecular), $cm^3 mol^{-1} s^{-1}$ (bimolecular).

Reaction	k	Refs.
Cyclohexene \leftrightarrow 2-cyclohexenyl + H	$5.01 \times 10^{15} \exp(-41140/T[K])$	[30]
1,3-Butadiene \leftrightarrow $C_2H_2 + C_2H_4$	$7.00 \times 10^{12} \exp(-33790/T[K])$	[31]
1,3-Butadiene \leftrightarrow $C_4H_4 + H_2$	$2.50 \times 10^{15} \exp(-47680/T[K])$	[32]
1,3-Butadiene \leftrightarrow $i-C_4H_5 + H$	$5.70 \times 10^{36} T[K]^{-6.27} \exp(-56570/T[K])$	[33]
1,3-Butadiene \leftrightarrow $n-C_4H_5 + H$	$5.30 \times 10^{44} T[K]^{-8.62} \exp(-62240/T[K])$	[33]
$C_2H_4 + Ar \leftrightarrow C_2H_2 + H_2 + Ar$	$2.61 \times 10^{16} \exp(-34130/T[K])$	[18]
$C_2H_4 + Ar \leftrightarrow C_2H_3 + H + Ar$	$2.59 \times 10^{17} \exp(-48590/T[K])$	[34]

indicating that a point measurement behind a given reflected shock wave is insensitive to the activation energy of the rate constant for *Reaction 1* used to fit the measured ethylene mole fraction time history.

Since the rate of ethylene decomposition spans four orders of magnitude across the temperature range in this study, various strategies were deployed to optimize measurements at different temperatures. At low temperatures, due to the slow decomposition of ethylene, driver inserts [22] and driver gas tailoring [23] were used in order to extend the measurement test time to 4 ms and to eliminate non-ideal effects typically present in shock tubes at long test times. In addition, the laser beam was passed twice through the diameter of the shock tube at the measurement location in order to double the sensitivity of the ethylene diagnostic. Finally, an initial concentration of cyclohexene of 3% was used in order to generate measurable concentrations of ethylene throughout the test time. At low post-reflected-shock temperatures, temperature remains constant throughout the test time due to the low conversion of cyclohexene. Based on the accuracy of the shock speed measurement system, which is discussed at the end of this section, and the uniformity in pressure observed throughout the test time, which is shown in Figure 2, it is estimated that temperature uncertainty throughout the test time in low post-reflected-shock temperature experiments is $\pm 0.8\%$.

At high temperatures, endothermic decomposition of cyclohexene causes a slight temperature drop as a function of time behind the reflected shock wave. This affects measurements of ethylene mole fraction due to the temperature dependence of the absorp-

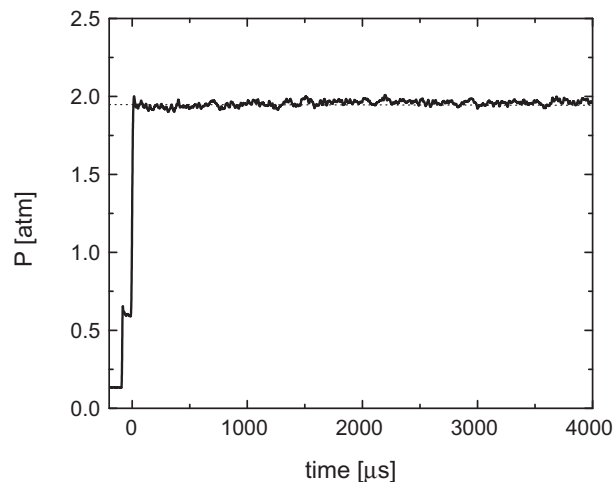


Figure 2. Pressure trace for a representative experiment using driver gas tailoring and driver inserts. Post-reflected-shock conditions: $T = 985$ K, $P = 1.93$ atm, $x_{\text{cyclohexene}} = 3\%$.

tion cross-sections. Furthermore, temperature variations as low as 5 K behind the reflected shock wave must be taken into account while modeling the ethylene time-histories in order to account for the time-evolution of the rate constant for *Reaction 1*, which is highly temperature dependent. In order to minimize the uncertainty in the measured rate constant associated with temperature changes behind the reflected shock wave, dilute 0.333% mixtures of cyclohexene were used in high post-shock-temperature experiments. Furthermore, rate constants were inferred by examining ethylene formation at early times when cyclohexene conversion was below 30% and significant temperature change did not occur. On timescales where data were fitted to simulations, temperature dropped by no more than 15 K, and absorption cross-sections were corrected using simulated temperature time histories, as described in previous work [24]. At the conditions studied, the magnitude of the temperature correction on ethylene mole fraction measurements was less than 5%. Furthermore, by fitting the rate of ethylene formation using simulations with a temperature-dependent rate constant for *Reaction 1*, simulations provide good estimates for the time-evolution of the rate constant for *Reaction 1* throughout the fitting time. Since virtually all kinetic reactions in this study occur via *Reaction 1*, the fractional conversion of cyclohexene to ethylene is directly related to temperature variations via the adiabatic constraint, an appropriate gas-dynamic model of the shock tube, and accurate knowledge of the thermodynamic properties of the three major species present in the shock tube. Therefore kinetic simulations which are constrained to fit the measured ethylene time-histories accurately predict the corresponding temperature changes inside the shock tube. The uncertainty in the measured rate constant at high temperatures associated with the choice of gas-dynamic model was considered in detail, based on previous work [24] involving simulation of temperature changes behind reflected shock waves due to endothermic reactions. This uncertainty can be quantified by fitting the measured ethylene time-histories using both constant pressure and constant volume gas-dynamic models, which result in measured values of the rate constant for *Reaction 1* that differ by no more than 2%.

The uncertainty in the initial temperature behind the reflected shock wave, which is discussed in the following paragraph, for dilute experiments performed at high post-reflected-shock temperatures is $\pm 0.35\%$. Measurements were not performed at temperatures above 1300 K because the rapid formation of ethylene could not be measured accurately due the limited time resolution of the ethylene diagnostic, which is approximately 7 μs .

The uncertainty of the initial post-reflected-shock temperature is primarily dependent on the uncertainty in the extrapolated incident shock speed at the endwall of the shock tube. Incident shock speeds are calculated by monitoring the arrival times of the incident shock wave at a series of five pressure transducers near the endwall of the shock tube, which produce four measurements of the average incident shock speed between adjacent pairs of fast-response pressure transducers. Measured incident shock speeds show a linear attenuation rate of no more than 0.8%/m. Incident shock speed measurements between a given pair of pressure transducers do not deviate from the linear fit used to extrapolate the measured incident shock speeds to the endwall by more than 0.17%. Therefore it is estimated that the incident shock speed at the endwall is known to within $\pm 0.13\%$, which contributes to an uncertainty in temperature behind the reflected shock wave of $\pm 0.26\%$. These estimates are consistent with the absolute measured timing error of the incident shock speed measurement system, which was characterized by mounting all five pressure transducers at the same axial location in the shock tube and monitoring the time response of the signal rise caused by the incident shock wave. It was observed that the signals in all five pressure transducers reached the trigger level of the shock speed counters within

1.1 μs of each other. Given that the typical time interval for an incident shock speed measurement between a pair pressure transducers at the conditions in this study is 500 μs , a 1.1 μs timing error corresponds to an overall 0.22% uncertainty in the incident shock velocity. This analysis is consistent with analysis of the uncertainty in the post-reflected-shock temperature performed by Herbon [25]. Furthermore, it is consistent with laser-absorption measurements of temperature behind reflected shock waves performed in our laboratory by Farooq et al. [26], which indicate that the mean deviation between the measured and calculated temperature was less than 0.11%. It is noted that the uncertainties in the post-reflected-shock temperature reported here are primarily systematic and are significantly greater than those suggested by the scatter in the experimental data. The mean deviation in the rate constant measurements from the Arrhenius fit in this study is 4.3%, which based on the temperature sensitivity of the measured rate constant suggests that the random uncertainty in the temperature is on the order of 0.15%.

Due to the large number of vibration modes in cyclohexene, the post-reflected-shock temperature is also sensitive to the cyclohexene concentration in the shock tube, which is known to within $\pm 1.5\%$ of the manometrically calculated value. In dilute experiments using 0.333% cyclohexene, the uncertainty in the initial cyclohexene mole fraction has a negligible effect on the uncertainty in the post-reflected-shock temperature. However, in experiments using 3% cyclohexene, the uncertainty in the cyclohexene concentration as well as its thermodynamic properties contributes approximately $\pm 0.2\%$ to the uncertainty in the post-reflected-shock temperature.

4. Results and discussion

A representative measurement and simulation of the ethylene mole fraction time-history is shown in Figure 3. The data exhibit low noise and simulations show excellent sensitivity to the target rate constant. The characteristic shape of ethylene formation as a function of time is in excellent agreement between measurements and simulations even at high temperatures, which indicates that simulations provide good estimates for the temperature time-history behind the reflected shock wave throughout the fitting time. Measurements of the rate constant for Reaction 1 at various temperatures are presented in Table 2 and plotted in Figure 4. Data in the current study were acquired from 0.8 to 3.7 atm and show no pressure dependence across the temperature range studied. Measurements are best-fit by the Arrhenius expression:

$$k[\text{s}^{-1}] = 4.84 \times 10^{14} \exp(-31900[\text{K}]/T)$$

The maximum uncertainty in the rate constant measurements in the current work is approximately $\pm 36\%$ at temperatures below 1000 K, $\pm 21\%$ at temperatures from 1000 to 1200 K, and $\pm 19\%$ at temperatures above 1200 K. Due to the large temperature sensitivity of the rate constant for Reaction 1, the dominant contributor to the uncertainty in the measured rate constants is the uncertainty in the post-reflected-shock temperature described in detail in the Experimental Setup section. Overall uncertainties were calculated by linearly adding the uncertainties due to the following factors (brackets indicate the contribution to the overall uncertainty in the rate constant for Reaction 1): temperature ($\pm 26\%$ low T, $\pm 9\%$ high T), pressure ($\pm 1.5\%$ low T, $\pm 0.7\%$ high T), initial cyclohexene mole fraction ($\pm 1.5\%$), absorption cross-section of ethylene and 1,3-butadiene ($\pm 2\%$), gas-dynamic model in simulations ($\pm 1.5\%$, high T only), fitting uncertainty ($\pm 2.0\%$ nominally, $\pm 5\%$ low T), effect of secondary reactions on kinetic modeling ($+2.0\%$, high T only), effect of secondary reactions on measurement of ethylene (-2.5% , high T only).

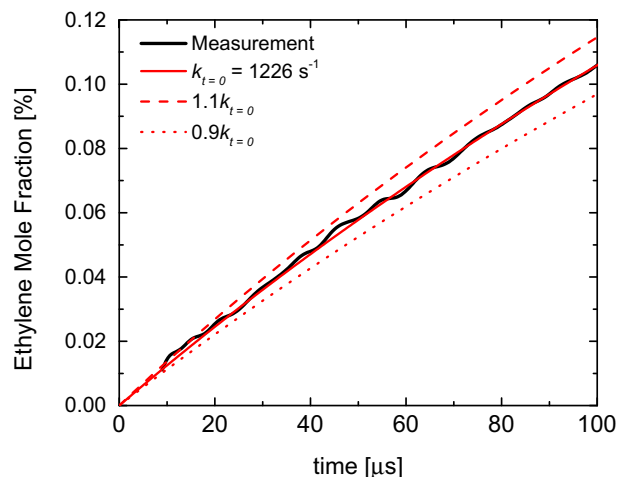


Figure 3. Representative measurement and simulation of ethylene mole fraction time histories. Reaction rate constant for simulations specified at the post-reflected-shock temperature. Note that the rate constant changes slightly throughout the measurement time due to a small decrease in temperature. 1% cyclohexene diluted in argon. Post-reflected-shock conditions: $T = 1192 \text{ K}$, $P = 3.52 \text{ atm}$.

Table 2

Summary of the rate constant measurements for Reaction 1. All mixtures are balanced in argon.

$x_{\text{cyclohexene}} (\%)$	T [K]	P [atm]	$k [\text{s}^{-1}]$
1.00	1235	1.91	2830
	1172	2.04	764
	1080	2.11	68
	1027	2.11	15.0
	1087	3.72	92
	1192	3.52	1230
	1227	1.89	2490
	1087	3.69	100
	1043	3.80	26.4
	0.333	1265	1.93
	1276	3.49	6840
	1300	1.24	9610
	1126	1.94	245
3.00	997	2.03	5.7
	1042	1.94	23.6
	959	0.82	1.77
	975	0.88	3.0
	985	1.93	4.2

Measurements in the current work exhibit lower scatter and uncertainty compared to previous studies. Uncertainties in the reaction rate constant measurements from past studies are generally on the order of \pm a factor of 1.5–3.0. Previous studies show good agreement with the current work at temperatures below 1250 K, and there exist greater discrepancies between studies at higher temperatures. Though past studies offer a variety of explanations for the observed discrepancies at high temperatures, they are not discussed in detail here because the focus of discussion in the current work is at temperatures from 950 to 1100 K where Reaction 1 is typically used as a reference. In this temperature range, there is variable agreement between studies for this measured rate constant, as shown in Figure 5. It is noted that the Arrhenius rate constant expressions for some previous studies shown in Figure 5 have been extrapolated beyond the temperature range where measurements were performed. Figure 5 demonstrates that measurements by Barnard et al. [6] and Lewis et al. [27] are in good agreement with the current study. Lewis et al. [7] do not propose a new reaction rate constant expression for Reaction 1 and so it is not presented here. However, rate constant expressions for Reaction 1

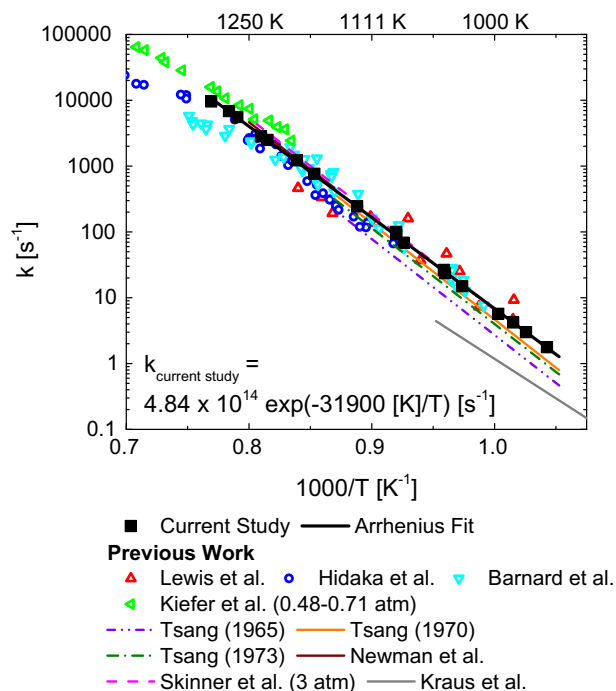


Figure 4. Measurements of the rate constant for cyclohexene decomposition in the current study, as well a comparison with measurements from the literature. Pressure range in the current study is 0.8–3.7 atm. Pressure in past studies is indicated if measurements were performed at multiple pressures. Uncertainties in the current study are approximately equal to the height of the data points.

by Tsang (1965) [2] and Tsang (1970) [3] are up to 38% and 64% lower, respectively, compared to measurements in the current study. Furthermore, rate constant expressions by Tsang (1973) [4], which are referred to as the ‘best’ estimate among the studies by Tsang [2–4] and are also the most commonly used in chemical thermometry and comparative rate studies [28,29], are up to 45% lower than the measurements in the current work. Nonetheless, it is noted that rate constant expressions from the current study and from the studies by Tsang [2–4] likely lie within each other’s combined uncertainties. Finally, measurements by Kraus et al. [12] are up to an order of magnitude lower compared to those in the current and other studies. It is noted that the lack of an observed pressure dependence of the rate constant for *Reaction 1* between 0.8 and 3.7 atm in the current work indicates that the discrepancies between the past studies discussed here are not caused by variations in experimental pressure. Analysis of the pressure dependence of *Reaction 1* in previous work [6,8] confirms that all studies discussed above should not exhibit any significant pressure dependence at temperatures below 1200 K.

The significance of the discrepancies in the recommended rate constant expressions for *Reaction 1* can be quantified by examining the corresponding variations in the inferred temperature using the chemical thermometry method. As shown in Figure 6, the inferred temperature using the rate constant expression from the current work compared to using the rate constant expressions from studies by Tsang [2–4] is up to 30 K lower at temperatures from 950 to 1100 K. Although these modest temperature discrepancies are not unexpected given the uncertainties in the individual rate constant measurements for cyclohexene decomposition, they may have significant implications for other chemical kinetic studies. The temperature discrepancies reported here are in excellent agreement with a recent study by Heyne et al. [21], which indicates that temperature measurements from 950 to 1000 K in a flow reactor using a thermocouple are 17 K lower compared to calculated

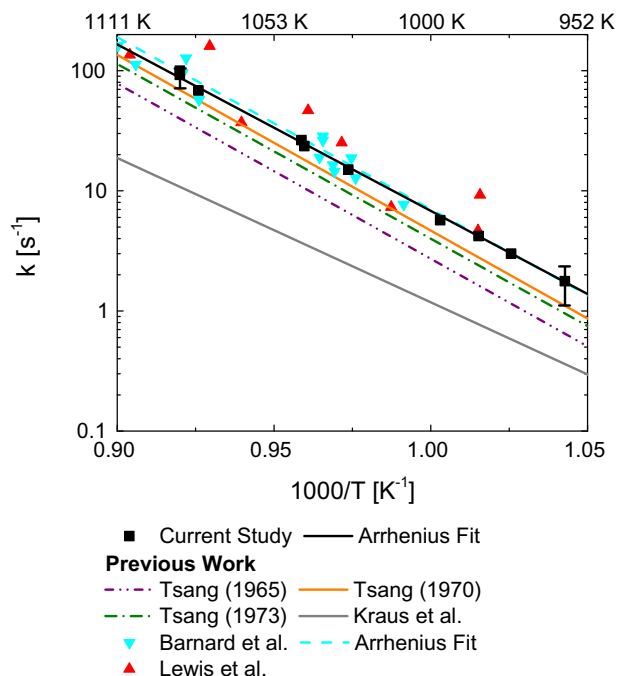


Figure 5. Subset of measurements of the rate constant for cyclohexene decomposition in the current study, as well as comparisons with measurements from the literature, in the temperature range where cyclohexene is commonly used as a reference. Pressure range in the current study is 0.8–3.7 atm.

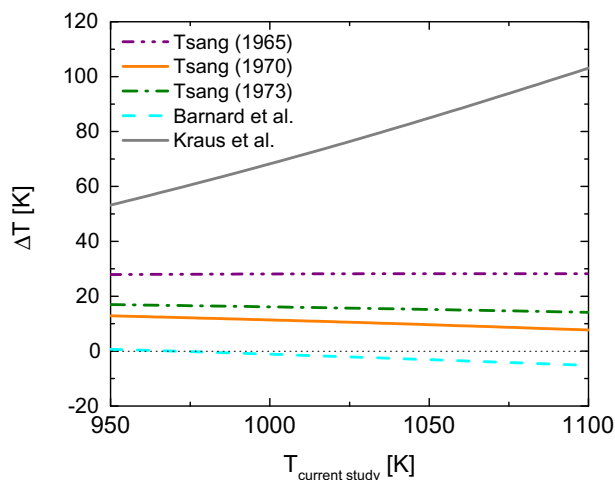


Figure 6. Difference in the inferred temperature using chemical thermometry. $\Delta T = T_{\text{previous work}} - T_{\text{current work}}$, where $T_{\text{current work}}$ is the inferred temperature using the rate constant expression for *Reaction 1* from the current study, and $T_{\text{previous work}}$ is the inferred temperature using the rate constant for *Reaction 1* from previous work.

values using cyclohexene as a chemical thermometer, when based on the rate constant for cyclohexene decomposition from Tsang (1973) [4]. It is noted that errors in chemical thermometry or comparative rate methods associated with variations in the rate constant for *Reaction 1* are primarily systematic. Therefore, rate constant measurements from previous studies can be corrected retroactively using the updated rate constant expression, if desired.

5. Conclusions

The rate constant for the reaction cyclohexene \rightarrow ethylene + 1,3-butadiene was measured between 950–1300 K and

0.8–3.7 atm. No pressure dependence was observed at these conditions. Though measurements show fair agreement with previous studies, we believe this is the most accurate determination of the rate constant for the target reaction to date. Discrepancies with previous work in the measured rate constant for the target reaction correspond to variations in the inferred temperature using the chemical thermometry method of approximately 20 K.

Acknowledgments

The kinetics aspects of this research were supported by the U.S. Department of Energy, Office of Basic Energy Sciences, with Dr. Wade Sisk as contract monitor. Laser diagnostics development was supported by AFOSR, with Dr. Chiping Li as contract monitor. The authors would like to thank Prof. Frederick Dryer of Princeton University for motivating the work.

References

- [1] W. Tsang, *J. Chem. Phys.* 40 (1964) 1171.
- [2] W. Tsang, *J. Chem. Phys.* 42 (1965) 1805.
- [3] W. Tsang, *Int. J. Chem. Kinet.* 2 (1970) 311.
- [4] W. Tsang, *Int. J. Chem. Kinet.* 5 (1973) 651.
- [5] M. Uchiyama, T. Tomioka, A. Amano, *J. Phys. Chem.* 68 (1964) 1878.
- [6] J.A. Barnard, T.K. Parrott, *J. Chem. Soc., Faraday Trans. 1* (72) (1976) 2404.
- [7] D.K. Lewis, J. Bergmann, R. Manjoney, R. Paddock, B.L. Kalra, *J. Phys. Chem.* 88 (1984) 4112.
- [8] J.H. Kiefer, J.N. Shah, *J. Phys. Chem.* 91 (1987) 3024.
- [9] G.B. Skinner, D. Rogers, K.B. Patel, *Int. J. Chem. Kinet.* 13 (1981) 481.
- [10] C.G. Newman, H.E. O'Neal, M.A. Ring, F. Leska, N. Shipley, *Int. J. Chem. Kinet.* 11 (1979) 1167.
- [11] L. Kuchler, *Trans. Fara. Soc.* 35 (1939) 874.
- [12] M. Kraus, M. Vavruska, V. Bazant, *Collect. Czech. Chem. Commun.* 22 (1957) 484.
- [13] R.V. Smith, A.S. Gordon, *J. Phys. Chem.* 65 (1961) 1124.
- [14] Y. Hidaka, T. Chimori, S. Shiba, M. Suga, *Chem. Phys. Lett.* 111 (1984) 181.
- [15] I. Stranic, D.P. Chase, J.T. Harmon, S. Yang, D.F. Davidson, R.K. Hanson, *Combust. Flame* 159 (2012) 516.
- [16] M.A. Oehlschlaeger, D.F. Davidson, R.K. Hanson, *J. Phys. Chem. A* 108 (2004) 4247.
- [17] P.N.N. Laboratory, Vapor Phase Infrared Spectral Library (2012) <https://secure2.pnl.gov/nsd/nsd.nsf/Welcme>.
- [18] W. Ren, D.F. Davidson, R.K. Hanson, *Int. J. Chem. Kinet.* 44 (2012) 423.
- [19] G.L. Pilla, D.F. Davidson, R.K. Hanson, *Proc. Combust. Inst.* 33 (2011) 333.
- [20] E.J. Silke, W.J. Pitz, C.K. Westbrook, M. Ribaucour, *J. Phys. Chem. A* 111 (2007) 3761.
- [21] J.S. Heyne, F.L. Dryer, *J. Phys. Chem. A* 117 (2013) 5401–5406.
- [22] Z. Hong, G.A. Pang, S.S. Vasu, D.F. Davidson, R.K. Hanson, *Shock Waves* 19 (2009) 113.
- [23] Z. Hong, D.F. Davidson, R.K. Hanson, *Shock Waves* 19 (2009) 331.
- [24] I. Stranic, S.H. Pyun, D.F. Davidson, R.K. Hanson, *Combust. Flame* 159 (2012) 3242.
- [25] J.T. Herbon, Shock Tube Measurement of CH₃ + O₂ Kinetics and the Heat of Formation of the OH Radical, Stanford University, Stanford, CA 2004.
- [26] A. Farooq, J.B. Jeffries, R.K. Hanson, *Appl. Phys. B* 96 (2009) 161.
- [27] D. Lewis, M. Keil, M. Sarr, *J. Am. Chem. Soc.* 94 (1974) 4398.
- [28] A. Lifshitz, *Shock Waves in Chemistry*, Marcel Dekker Inc., New York and Basel, 1981.
- [29] I.A. Awan, D.R. Burgess Jr., W. Tsang, J.A. Manion, *Int. J. Chem. Kinet.* 44 (2012) 351.
- [30] A.M. Dean, *J. Phys. Chem.* 89 (1985) 4600.
- [31] S. Peukert, C. Naumann, M. Braun-Unkhoff, *Z. Phys. Chem.* 223 (2009) 427.
- [32] Y. Hidaka, T. Higashihara, N. Natsuhiko, M. Hiromitsu, N. Takuji, K. Hiroyuki, *Int. J. Chem. Kinet.* 28 (1996) 137.
- [33] H. Wang, M. Frenklach, *Combust. Flame* 110 (1997) 173.
- [34] D.L. Baulch et al., *J. Phys. Chem. Ref. Data* 23 (1995) 847.