A Shock Tube Study of H Atom Addition to Cyclopentene

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Abstract

We report shock tube studies of the kinetics of H atom addition to cyclopentene and modeling of the subsequent decomposition of cyclopentyl. Hydrogen atoms were generated with thermal precursors in dilute mixtures of cyclopentene and a reference compound in argon. Addition of H to the double bond leads to a cyclopentyl radical that rapidly ring opens and decomposes to ethene and allyl radical. The process was monitored by post-shock gas chromatographic analysis of ethene and rate constants determined relative to H atom displacement of methyl from 1,3,5-trimethylbenzene (135TMB). At (863 to 1167) K and (160 to 370) kPa we find:

 $k(\text{H+cyclopentene} \rightarrow \text{ethene+allyl})/k(\text{H+135TMB} \rightarrow m\text{-xylene+CH}_3) = 10^{-0.196} \exp(1995 \text{ K/T}),$

and, with $k(H+135TMB \rightarrow m$ -xylene+methyl) = 6.70 x 10^{13} exp(-3255 K/T) cm³mol⁻¹s⁻¹, we obtain:

 $k(H + cyclopentene \rightarrow ethene + allyl) = 4.27 \times 10^{13} \exp(-1260 \text{ K/T}) \text{ cm}^3 \text{mol}^{-1}\text{s}^{-1}$

Using experimental values of about 3:1 for the ratio of C-C to C-H beta scission in cyclopentyl radicals and a corresponding Transition-State-Theory/Rice-Ramsberger-Kassel-Marcus (TST/RRKM) model, the high pressure rate expression for addition of H to cyclopentene at (863 to 1167) K is derived as:

 k_{∞} (H+cyclopentene \rightarrow cyclopentyl) = 5.37 x 10¹³ exp(-1213 K/T) cm³mol⁻¹s⁻¹

Combined with literature results from lower temperatures and a fitted TST model, the rate expression between 298 K and 2000 K is determined as:

 k_{∞} (H+cyclopentene \rightarrow cyclopentyl) = 9.1 × 10⁷ T^{1.78} exp(-324 K/T) cm³ mol⁻¹s⁻¹;

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 scission in cyclopentyl radicals to maintain established trends in H addition rates. This conflicts with current computed values and those used in existing kinetics models of cyclopentane combustion. We additionally report and discuss minor observed channels in the decomposition of cyclopentene, including formation of 1,4-pentadiene, (E/Z)-1,3-pentadiene, 1,3-butadiene, and the direct elimination of H₂ from cyclopentene to give cyclopentadiene.

Key Words: kinetics, hydrogen atoms, cyclopentyl, 1,4-pentadiene, 1,3-pentadiene, 1,3-butadiene.

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1. INTRODUCTION

This paper is concerned with the determination of rate constants for addition of H atoms to cyclopentene and the relationship of this process to the subsequent kinetics of cyclopentyl radical decomposition. Cyclopentene (CPE) is the smallest hydrocarbon having an unsaturated C_5 ring. A combustion intermediate and component of some fuels, it represents a prototypical species useful in understanding the expected behavior of larger analogs. Our interest is related to the development of reliable kinetic models for the combustion and pyrolysis of hydrocarbon ring structures. Such 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. Of relevance are unsaturated five and six membered ring compounds that are products of some chemical pathways. In competition with their oxidation, subsequent further reaction of these ring systems with small radicals leads to polycyclic aromatic hydrocarbons (PAH's), finally terminating with particulate soot,¹⁻⁴ which is an environmental and regulatory concern. Benchmark information on the chemistry of the base ring structures provides key data needed to reliably extend the kinetic models to larger systems.

Addition of H to cyclopentene forms the cyclopentyl radical, which at higher temperatures is well-established to undergo ring opening and ensuing decomposition to ethene and allyl radical.⁵⁻¹³ Ring opening competes with the re-ejection of hydrogen atom, the kinetics of which is related to H addition through detailed balance. The overall decomposition is:

cyclopentene (CPE) + H
$$\rightarrow$$
 ethene + allyl (R1)

The process is depicted in Scheme 1 and is comprised of three elementary reactions, R2 to R4:

$$cyclopentene (CPE) + H \rightleftarrows cyclopentyl$$
(R2)

$$cyclopentyl \rightleftarrows pent-4-en-1-yl \tag{R3}$$

pent-4-en-1-yl
$$\rightleftharpoons$$
 ethene + allyl (R4)

Although the mechanism of cyclopentyl chemistry is established, there is conflicting information on the various rate constants. It is the balance of the various elementary reactions that determines the overall behavior under conditions of interest. An accurate determination of the H addition rate constant, in concert with available information on branching ratios and thermodynamic properties, will significantly limit the kinetic possibilities.



Scheme 1: Decomposition of CPE induced by addition of H atoms.

The present studies span temperatures of 860 K to 1170 K, where there are no direct determinations of the kinetics of H atom addition to CPE. Previous experimental work has been limited to a few studies at lower temperatures. Scherzer *et al.*¹⁴ reported in 1990 some mechanistic results on the H + cyclopentene reaction using a discharge flow system at 298 K, but did not determine rate constants. The sole kinetic study of which we are aware is the 2000 publication of Clarke *et al.*¹⁵ who used a discharge flow reactor equipped with resonance fluorescence detection of H to obtain overall reaction rates of H with cyclopentene and several other olefins at temperatures of 298 K to 370 K.

There are various related studies that will form an interesting basis for comparison. Tsang, in his 2006 model of pent-1-en-5-yl \rightarrow cyclopentyl chemistry, estimated rate constants for most of the elementary reactions in Scheme 1, including addition of H to cyclopentene. In 2008 Sirjean *et al.* used quantum chemical calculations at the CBS-QB3 level of theory to develop a rate expression for C-H bond scission in cyclopentyl radical. More recently we have directly measured the branching between cyclopentene and ethene products in the decomposition of cyclopentyl radical under conditions similar to the present experiments.⁹ This information will be used herein to convert our primary measurements to a reliable rate expression for the rate of the H addition reaction. Relevant to k_{-3} (Scheme 1), Wang *et al.*¹⁶ in 2015 derived structure activity rate estimation rules for ring closure in C₄ to C₈ alkenyl radicals. Herbinet *et al.*⁴ 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.*¹⁷ 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. In the present work, we use a single pulse shock tube and 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. We separately report and discuss new information on minor channels observed in the decomposition of cyclopentene. Results are discussed in the context of current models of cyclopentane pyrolysis and combustion and some incompatibilities are noted.

2. EXPERIMENTAL¹⁸

Experiments are carried out in a heated single pulse shock tube configured to have reaction times of (500 ± 50) µs. Details of the instrument and experimental procedures can be found in earlier publications.¹⁹⁻²¹ Shock tubes have reaction times so short that species cannot diffuse to the wall during reaction, thus ensuring isolation of the gas phase processes. In the current studies, reactants are highly diluted in a bath gas of argon and we use small quantities of a precursor [\approx 50 µL/L (ppm)] to create a limited number of H atoms in the presence of much larger quantities (\approx 10,000 µL/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. Contributions from radical chains and secondary chemistry are minimized by the dilute conditions, the use of a scavenger, and the short residence times. Post-shock analysis relates distinct products to relative reaction rates. Species are quantitated with high accuracy using gas chromatography with flame ionization and mass spectrometric detection (GC/FID/MS). Absolute rate constants are derived relative to the reference reaction.

Shock temperatures and corresponding pressures ranged from 863 K to 1167 K and 160 kPa to 370 kPa, respectively. Product analyses used a Hewlett Packard 6890 N GC equipped with twin flame ionization detectors (FIDs) and an Agilent Technologies 5975 mass selective detector. GC analyses employed a Restek 30m x 0.53 mm i.d. Rt-Alumina (Aluminum oxide porous layer) capillary column for the lighter components (typically $\leq C_5$) and a J & W Scientific DB-1 30m x 0.53 mm i.d. fused silica capillary column for the larger species. The oven was initially cooled

with chilled nitrogen gas and the temperature ramped during the analysis from 213 K to 453 K (-60 °C to 180 °C). An Agilent microfluidic splitter (Dean's Switch) was used to channel the sample eluting from the DB-1 column to both the MS and FID detectors to allow simultaneous identification and the quantification of the components.

Product concentrations are based on the FID analyses, with the MS used primarily to confirm product identities. Molar FID responses of the C₁ to C₉ species were determined from standard samples. Including possible systematic errors, we estimate the analytical uncertainty (1 σ) for the main products to be about 3 %. We lacked samples of the larger recombination products and uncertainties for these compounds are estimated to be about 6 %, increasing to about 12 % near the limits of detection, typically about 0.01 µL/L. As noted in the product table given in Supporting Information, the quantitation of some minor products at low conversions was limited by corrections to the FID peak areas due to backgrounds present in the unshocked mixtures.

Generation of H atoms. We have used three different methods to produce H atoms. Thermolysis of hexamethylethane (HME) is effective at temperatures greater than ≈ 1000 K. Fission of the central C-C bond is the overwhelming unimolecular process and results in the production of H atoms and a stable isobutene coproduct:

hexamethylethane
$$\rightarrow 2 tert$$
-butyl (R5)

$$tert$$
-butyl \rightarrow isobutene + H (R6)

A minor side process generates propene at levels of 3.5 % of isobutene,^{20,22} necessitating a welldefined and usually small correction to any propene attributed to other reactions the system. HME is less useful as a source of H below 1000 K, where k_5 is small. To probe lower temperatures, a few experiments were conducted with mixtures containing small amounts ($\approx 25 \,\mu$ L/L) of *tert*-butyl peroxide (tBPO) and a large amount of H₂ ($\approx 20 \,\%$), which leads to H atoms via the following sequence:

tert-butyl peroxide
$$\rightarrow 2 (CH_3)_3C-O \rightarrow 2 \text{ acetone} + 2 CH_3$$
 (R7)

$$CH_3 + H_2 \rightarrow CH_4 + H$$
 (R8)

Decomposition of tBPO is rapid at our temperatures and is essentially a pulse source of methyl radicals and acetone,²¹ the latter of which is stable. The subsequent reaction of methyl with H₂ is relatively slow, however, and the production of H atoms is limited by loss of methyl radicals to side reactions, primarily self-recombination and abstraction of H from CPE or the inhibitor. A more effective source of H atoms at low temperatures proved to be the decomposition of 2-iodopropane. This compound 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:

2-iodopropane
$$\rightarrow$$
 propene + HI (R9)

2-iodopropane
$$\rightarrow i$$
-C₃H₇ + I (R10)

$$i-C_3H_7 \rightarrow \text{propene} + H$$
 (R11)

Both pathways yield propene, so they cannot be distinguished based on that product. Weber *et al.*²³ have reported that the C-I bond fission fraction is 0.30 ± 0.05 of total decomposition between 770 K and 1100 K, in good agreement with values determined by Miyosyhi *et al.*²⁴ at higher temperatures. These fractions are smaller than branching values of about 0.75 found for the primary iodides²³⁻²⁵ but are sufficient to generate useful quantities of H atoms. Because our kinetic parameters for H addition are derived from relative product amounts, the exact branching ratio of R9 to R10 is irrelevant for current purposes.

Shock conditions. Shock temperatures are determined by following the extent of an appropriate unimolecular reaction that has well-known rate parameters. This method of temperature determination in shock tube studies has been extensively validated.²⁶⁻²⁸ In the present work we use the decomposition of hexamethylethane as the temperature standard at temperatures above ≈ 1000 K. Rate parameters, $k_4 = 3.0 \times 10^{16} \exp(-34400 \text{ K/T}) \text{ s}^{-1}$, are taken from the work of Tsang.^{26,28} For investigations at lower temperatures we use the decomposition of chlorocyclohexane (CCH), taking $k(\text{CCH} \rightarrow \text{cyclohexene} + \text{HCl}) = 10^{14.33} \exp(-25950 \text{ K/T}) \text{ s}^{-1}$ from our study and evaluation of several temperature standards.²⁸ Conversion fractions of the temperature standards are based on formation of the stable product olefins at degrees of conversion <10 % and by averaging the product and total loss values at larger conversions. Overall, we estimate the 1 σ uncertainties in the relative and absolute temperatures to be about 0.5 % and 1 %, respectively.

H atom kinetics and radical scavenger. In the present work, the rate constants for the reaction of H with CPE are determined relative to known values for the reaction of H with 135TMB. Attack of H on 135TMB leads either to H_2 and dimethylbenzyl radical (DMB) or displacement of methyl to give *m*-xylene:

$$H + 135TMB \rightarrow H_2 + dimethylbenzyl (DMB)$$
 (R12)

$$H + 135TMB \rightarrow CH_3 + m$$
-xylene (R13)

Near 1000 K the branching is about 2:1 in favor of abstraction.^{29,30} DMB has no low energy decomposition paths and the resonance stabilized radical does not readily abstract H from closed shell molecules to propagate radical chains. It terminates radical chains through recombination reactions, thus limiting secondary chemistry and allowing the initial chemical processes to be isolated. The displacement reaction (R13) is a convenient rate reference for reactions of H atoms because the *m*-xylene product is stable, easily quantitated, and is not commonly formed by other processes. In the current study and previous related work we use the rate parameters of Tsang *et al.*,³⁰ $k(H + 135TMB \rightarrow m$ -xylene + CH₃) = $6.7 \times 10^{13} \exp(-3255/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Near 1000 K, these rate constants are about 10 % larger than those later derived by Sheen *et al.*³¹ in a reanalysis of the H + propene/135TMB system using a detailed chemical kinetic model and spectral uncertainty propagation and minimization techniques. At our temperatures the uncertainty in k_{13} is about a factor of $1.5.^{20,30}$ The determined relative rates are typically good to about 10 % and the existing database of rate constants measured relative to 135TMB provides valuable comparisons and a consistent scaling of absolute values.

Chemicals. The chemicals used were cyclopentene (CPE, 99 %, Aldrich), chlorocyclohexane (99 %, Aldrich), hexamethylethane (HME, 98 %, Aldrich), *tert*-butyl peroxide (tBPO, di-*tert*-butyl peroxide, 98 %, Aldrich), 2-iodopropane (99 %, Aldrich), and 1,3,5-trimethylbenzene (135TMB, 99 %, Aldrich). Argon (Matheson, 99.999 % high purity grade) was used as the bath gas. 135TMB was distilled to reduce a small background of *m*-xylene; the main remaining contaminants were other trimethylbenzene isomers. The main impurities in our cyclopentene sample were small amounts of cyclopentadiene, cyclopentane and pentadienes. The material was used without further purification in the studies with mixtures (A to E). In later work at lower temperatures utilizing 2-

iodopropane as the H atom source, the sample was redistilled to reduce the backgrounds of cyclopentadiene and 1,4-pentadiene.

3. RESULTS AND DISCUSSION

3.1 Overview of chemistry. Matheu et al.³² applied a mechanism-generating computer code to the H + cyclopentene addition reaction and identified 70 possible product channels; they concluded, however, that the chemistry is overwhelmingly dominated by the reactions shown in Scheme 1. Our data support this and we found no indications of other significant channels. Thus, addition of H to cyclopentene induces its decomposition and leads to ethene and allyl radical (R1). The reference reaction R13 generates *m*-xylene and methyl radical. Ethene and *m*-xylene are stable and are the important diagnostic species used to follow the H atom kinetics. The open-shell coproducts of R1 (allyl) and R13 (methyl) can undergo further reactions, including radical-radical recombinations, disproportionations, and H abstraction reactions. While we observe the expected products and mass balances are good, e.g. typically (85 to 90) % for allyl, the complexity of the chemistry increases uncertainties and these species are therefore not used to follow the kinetics. We also find products associated with our H atom precursors and temperature standards. Finally, cyclopentene is present in large excess and is observed to undergo a small amount of direct decomposition, mainly to cyclopentadiene and H₂. In the Appendix we provide a detailed examination of the side chemistry, including discussion of products formed at levels as low as about 1 % of the diagnostic species. Some of the cyclopentene chemistry has not been previously discussed in the literature. While it does not impact our measurement of the H addition kinetics, it is relevant to development of detailed kinetic models of cyclopentene pyrolysis and combustion. Shock conditions and product data from individual experiments are provided in the Supporting Information.

3.2 Studied Mixtures. Compositions of the studied mixtures are detailed in Table 1. HME was used as the H atom source in Mixtures A through D. The component concentrations were varied only modestly in mixtures A, B, and C, whereas Mixture D used an approximately 15x larger concentration of HME to generate measurable H atoms at lower temperatures ($< \approx 1020$ K) where HME decomposition is slow. As discussed in Section 2, limited H atom production in these

Mixture	HME	CCH	tBPO	H ₂	2-IC ₃ H ₇	CPE	135TMB
А	68	-	-	-	-	7970	16660
В	72	-	-	-	-	8100	16960
С	119	-	-	-	-	8510	16830
D	1010	53.0	-	-	-	10810	20650
E	-	100	24	2.00x10 ⁵	-	9070	17310
F	-	53.2	-	-	96.3	4525	9650

Table 1. Composition of mixtures (μ L/L) used in present study (remainder is Argon).

HME = hexamethylethane; CCH = chlorocyclohexane; tBPO = *tert*-butylperoxide; 2-IC₃H₇ = 2-iodopropane; CPE = cyclopentene; 135TMB = 1,3,5-trimethylbenzene

experiments led us to explore $tBPO/H_2$ (Mixture E) and 2-iodopropane (Mixture F) as low temperature H atom sources. Use of 2-iodopropane proved to be the most successful method and yielded useful data at temperatures as low as 860 K. The results from Mixtures D and E are nonetheless valuable in that they demonstrate an absence of systematic effects on the rate data.

3.3 Kinetics of H addition. Ethene formation is directly related to the overall reaction CPE + H \rightarrow ethene + allyl (R1). The rate of this reaction relative to 135TMB + H \rightarrow *m*-xylene + CH₃ (R13) is given by the molar yields of ethene and *m*-xylene normalized by the ratio of the reactants:

$$\frac{k_1}{k_{13}} = \frac{\left[ethene\right]_t}{\left[m\text{-xylene}\right]_t} \frac{\left[135\text{TMB}\right]_{\text{Avg}}}{\left[\text{CPE}\right]_{\text{Avg}}}$$
(Eq1)

In equation 1 the subscript *t* denotes concentrations of the diagnostic products at the end of the reaction time, while the subscript *Avg* denotes an average of the initial and final concentrations of the indicated reactant. Although H atom induced losses of 135TMB and CPE are negligible, we have still averaged the concentration of each reactant because of the slight loss of CPE (≈ 6 %) at the highest temperatures due to its unimolecular decomposition (mainly to cyclopentadiene + H₂; the unimolecular process is not a source of ethene, see Appendix). The averaging adjustment is minimal: differences relative to simply using the starting 135TMB/CPE ratio are negligible at lower temperatures and are only 3% at the highest temperatures studied. The relative rate data are plotted in Figure 1 and yield:

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



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 a correction for branching in the decomposition of the cyclopentyl radical (see text).

The given uncertainties are 2σ and represent precision only. Including systematic errors, the overall uncertainty (2σ) in the relative rate is estimated as about ± 15 %. With $k_{13} = 6.7 \times 10^{13}$ exp(-3255/T) cm³ mol⁻¹ s⁻¹,³⁰ we derive:

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

The uncertainty (2σ) 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, the experimentally observed rate constant for ethene formation, k_1 , represents the minimum possible value of k_2 . Assuming that essentially all H additions yield either ethene or cyclopentene as a stable olefin, k_1 is related to the high pressure limit, $k_{2(\infty)}$ by equation 2:

$$k_{2(\infty)} = \frac{\gamma + 1}{\gamma} k_1 \tag{Eq2}$$

where γ is the product ratio, $\gamma = [\text{ethene}]/[\text{CPE}]$, in the decomposition of the cyclopentyl radicals formed by R2. In previous work⁹ we have measured values of γ by creating cyclopentyl radicals

under dilute conditions and directly observing the ethene/CPE product ratio. Values of γ were found to be about 3 between 950 K and 1109 K and exhibit only a slight temperature dependence. The cyclopentyl radicals were created by abstracting H from cyclopentane and were assumed to have a thermal energy distribution. The data were modeled with a Rice Ramsberger Kassel Marcus/Master Equation (RRKM/ME) treatment implemented with ChemRate software.^{33,34} Species structures were derived from computations at the G3MP2B3 level of theory and computed vibrational frequencies were scaled by a factor of 0.96. Entropies were derived using the usual rigid rotator harmonic oscillator (RRHO) approximation, modified to account for internal rotations where appropriate. Enthalpies of formation of the closed shell molecules were based on experimental data from the literature, while preliminary transition state energies were derived from the computations. The initial model was then minimally tuned to match experimental data. Tuning typically consisted of slight empirical adjustment of the lowest frequency in the transition states (usually highly anharmonic modes) and small empirical changes in the reaction barriers. Details can be found in the previous publication.⁹ As further discussed below, we have slightly updated the 2011 model to better match additional literature information, and then used it to derive values of γ for the chemically activated cyclopentyl radicals formed in the current experiment. Using ChemRate, the initial source of cyclopentyl is defined as the H + CPE reaction, thus adding the C-H bond energy of about 145 kJ mol⁻¹ to the thermal energy of the initial radical. Values of γ for the thermal and chemically activated cases are computed to be very similar at our temperatures and pressures, with differences of only about 1 %. With γ derived thusly and $k_{2(\infty)}$ and k_1 related as above, $k_{2(\infty)}$ is found to be about 30 % larger than k_1 (Figure 1) and we find:

$$\frac{k_{2(\infty)}}{k_{13}} = 10^{-0.096 \pm 0.062} \exp[(2042 \pm 60) \text{ K/T}); 863 \text{ K to } 1167 \text{ K}$$

and

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

Figure 2 compares the present results with selected data from the literature. The only other kinetic study of H + cyclopentene appears to be that of Clarke *et al.*,¹⁵ who investigated the reaction at (298 to 370) K and (2.7 to 8.7) kPa using a flow reactor equipped with a microwave plasma to generate hydrogen atoms and a resonance fluorescence detector to monitor H-atom

decays. Abstraction of H is negligible at these temperatures^{20,35-38} and their results should pertain to the high-pressure rate constant for addition of H. They also report H addition rates for several



Figure 2. High pressure rate constants for addition of H to cyclopentene and selected alkenes. CPE = cyclopentene; Z2B = (Z)-2-butene; T = terminal site; NT = nonterminal site. The dotted and solid lines indicate the respective empirical and TST fits to the experimental CPE data (red data points with 2σ uncertainties). Results for butenes are as indicated; values for 1-butene²⁰ are multiplied by 2 to normalize the number of addition sites relative to CPE. References: 2000CDK = Clarke *et al.*¹⁵; 2017AM = Awan and Manion (unpublished work).

other alkenes that have been studied with direct methods by other investigators. In cases where multiple studies exist, the works show excellent agreement in the relative rate constants, and very good agreement in the absolute values. Based on these comparisons we estimate an overall uncertainty of 25 % in the absolute value of k_2 determined by Clarke *et al.* Although the present data and those of Clarke *et al.* agree within a factor of about two when using Arrhenius extrapolations, we feel the data are more compatible with slight upward curvature in the rate constant. An empirical fit of the form $AT^n \exp(-E/T)$ to the combined data spanning 298 K to 1167 K yields:

$$k_{2(\infty)} = 8.61 \times 10^{10} T^{0.874} \exp(-853 \text{ K/T}) \text{ cm}^3 \text{ mol}^{-1} \text{s}^{-1}$$
; 298 K to 1167 K

An alternative treatment is provided by our tuned transition-state theory (TST) model (Section 3.4), which yields:

$$k_{2(\infty)} = 9.09 \times 10^7 T^{1.783} \exp(-324 \text{ K/T}) \text{ cm}^3 \text{ mol}^{-1} \text{s}^{-1}$$
; 298 K to 2000 K

The TST model predicts greater curvature than the empirical fit and yields extrapolated rate constants that are about 30 % larger at 2000 K. Differences are less than 15 % between 298 K and 1200 K, with the TST fit providing slightly smaller rate constants at mid-temperatures where there are no data. For consistency with other rate constants in our model of cyclopentyl decomposition, we recommend use of the parameters from transition-state theory.

For comparison, we plot two other sets of high pressure limiting rate constants. The first are for addition of H to the terminal and non-terminal positions of 1-butene, with parameters taken from our recent measurement and evaluation.²⁰ The values near 1000 K were determined relative to the same reference reaction used here (R13), so relative rates should be self-consistent. The second are for addition of H to (*Z*)-2-butene, a non-cyclic olefin with an internal double bond. Results for (*Z*)-2-butene between 298 K and 370 K are from Clarke *et al.*¹⁵ while those near 1000 K are preliminary unpublished results from this laboratory (also based on R13). The data seem internally consistent and suggest that at both low and high temperatures the monoolefinic C₅ ring reacts somewhat faster than straight chain analogs having an internal double bond. On a per-site basis, rates of H addition to cyclopentene lie between those found for the terminal and non-terminal positions of 1-olefins.

We have derived the high pressure limiting rate constant for H atom addition to cyclopentene $[k_{2(\infty)}]$ using γ values (\approx 3) computed from our model fitted to experiment. Smaller values of γ would lead through equation 2 to larger values of $k_{2(\infty)}$. At the temperatures of our experiments, values of γ 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 trends in rates of H atom addition to olefins observed in our work on 1-butene²⁰ and 2-pentene,³⁹ and in numerous measurements at temperatures in the range of 250 K to 400 K,^{15,36-38,40,41} all of which show that addition to the terminal site of an alkene is significantly faster than to an alkyl substituted site. To maintain self-consistency in H atom addition rates, we suggest the reasonable lower limit of γ is about 1.5. This derived minimum is consistent with our previously measured γ values,⁹ but is obtained in an

independent manner. It represents a significant observation because, as we discuss later, γ values derived from computations and used in current kinetics models of cyclopentane combustion are all in the range of 0.3 to 0.8 near 1000 K. Our present measurements constrain the lower limit of

	Reaction	Log A	n	<i>E</i> /R	Log <i>k</i> ∞	Ref
				(K)	(1000 K)	
R2	cyclopentene + H \rightarrow cyclopentyl	7.96	1.78	324	13.16	This Work ^a
		13.19	0	1842	13.19	2015WVDb ^{c,42}
		13.82	0	2000	12.95	2006Tsa ¹⁰
		8.73	1.47	-91	13.18	2011ABT ⁹
R-2	cyclopentyl → cyclopentene + H	10.80	0.998	17486	6.21	This Work ^a
		11.95	0.69	18430	6.01	2017ATT ¹⁷
		12.68	0.847	17824	7.48	2008SGR ⁷
		11.80	0.46	16670	5.94	2006Tsa ¹⁰
		12.30	0.821	17138	6.33	2011ABT ⁹
R3	cyclopentyl \rightarrow pent-4-en-1-yl	12.31	0.677	17505	6.75	This Work ^a
		13.09	0.24	18138	5.93	2017ATT ¹⁷
		14.23	0	17361	6.69	2015WVDb ^{c,42}
		12.68	0.57	17326	6.87	2008SGR ⁷
		13.25	0.407	17506	6.87	2011ABT ⁹
		13.14	0	17260	5.64	1995HSW ⁴³
_		12.81	0.156	17139	5.83	2006Tsa ¹⁰
R-3	pent-4-en-1-yl \rightarrow cyclopentyl	9.45	0.716	8194	8.03	This Work ^a
		7.22	1.02	7146	7.17	2015WVDa ^{b,16}
		10.88	0	7750	7.51	2015WVDb ^{c,42}
		6.57	1.391	7202	7.62	2008SGR ⁷
		6.22	1.39	8631	6.64	2006Tsa ¹⁰
		8.08	1.05	7951	7.78	2003MG ³²
_		8.83	0.89	7733	8.15	2011ABT ⁹
R4	pent-4-en-1-yl \rightarrow ethene + allyl	10.82	0.774	10005	8.80	This Work ^a
		13.17	0	10417	8.65	2015WVDb ^{c,42}
		11.96	0.39	12376	7.76	2006Tsa ¹⁰
		10.98	0.73	9535	9.03	2011ABT ⁹
R-4	ethene + allyl \rightarrow pent-4-en-1-yl	3.98	2.40	5173	8.94	This Work ^a
		3.43	2.7	5686	9.06	2015WVDa ^{b,16}
		12.33	0	7397	9.12	2015WVDb ^{c,42}
		2.87	2.57	4627	8.57	2011ABT ⁹

Table 2. High pressure limiting rate parameters for elementary reactions of Scheme 1 from this work and literature sources; $k = A (T/K)^n exp(-E/T)$; units: cm³, mol⁻¹, s⁻¹, K.

^a Our parameters are fits to model *k*'s between 300 K and 2000 K and are consistent with detailed balance and our thermochemistry. Significant figures are given to accurately represent the model results and do not imply accuracy. See text for uncertainties. ^b Table 2 of that work. ^c Table S4 of that work.

 γ , but not the upper value; even a γ value of 100 would reduce the derived $k_{2(\infty)}$ by only 30 % and would not create obvious inconsistencies in rates of H atom addition.

3.4 TST and RRKM model. Our current model of H addition to cyclopentene and cyclopentyl decomposition uses the G3MP2B3 computations reported⁹ in 2011 with slight retuning to better

match additional data. The model now considers and fits the lower temperature results of Clarke *et al.*,¹⁵ whereas the 2011 model overpredicted those rate constants by a factor of about 2. In addition, the ring deformation mode in cyclopentene is now approximated as an internal (pseudo)rotation rather than a harmonic vibration. Parameters for this mode were selected empirically to enable a close match to the critically reviewed entropy of cyclopentene^{44,45} at 298 K and 1000 K. We have also updated the energy transfer parameters, now using $<\Delta E_{down}>/cm^{-1}$

 $K^{-1} = 0.675T$, where *T* is the temperature in Kelvin. This formulation is that deduced in our study of pressure dependence in the decomposition of *n*-pentyl radical⁴⁶ and gives $<\Delta E_{down}>$ values a factor of 2.3 greater than employed in 2011. This slightly changes the extrapolation to high pressure limit values, but the impact is minimal under our conditions where predicted falloff effects are small. Experimental rate constants for H addition span temperatures from 298 K to 1167 K. It was not necessary to include tunneling to fit these data, although we obtained fits of similar quality when employing a one-dimensional tunneling correction based on an asymmetric Eckart potential together with small simultaneous adjustments of the addition barrier. We have elected not to include this correction, given the limitations of the one-dimensional treatment,^{47,48} the absence of data in the tunneling-prevalent region below 298 K, and the semi-empirical nature of our fit. High pressure limiting rate expressions from our model for the six reactions of Scheme 1 are provided in Table 2 along with comparisons with other literature values. The complete current model is provided in the Supporting Information as an html file that can be read with a web browser or directly uploaded into ChemRate. We separately provide thermodynamic parameters of the model species in both tabular form and as NASA-format^{49,50} polynomials.

Relative and absolute rate constants for ring opening and C-H bond scission. Because ring opening is only mildly reversible at high temperatures, the ratio of ring opening to C-H scission (k_3/k_{-2}) differs only slightly from the experimentally measured⁹ values of γ , which have an estimated uncertainty of 16 % (2 σ). Absolute rate constants for ring opening are thus derivable from the presently measured rate constants for H addition to cyclopentene in conjunction with detailed balance and values of γ . We find:

$$k_{3(\infty)} = 4.68 \times 10^{14} \exp(-18240 \text{ K/T}) \text{ cm}^3 \text{ mol}^{-1} \text{s}^{-1}$$
; 863 K to 1167 K

The uncertainty in our absolute rate constant for H addition is about a factor of 1.5. The kinetics of the reverse C-H bond scission is less well defined due to uncertainties in the thermochemistry.

Our current model of cylcopentene was closely matched to the preferred entropies⁴⁴ at 298 K and 1000 K by approximating the inversion ring mode as an internal (pseudo)rotation. This reduces the computed value of $k_{-2}(1000 \text{ K})$ by about 25 % relative to the harmonic approximation used previously.⁹ Little is known about the analogous mode in cyclopentyl, but the resulting uncertainty in k_{-2} is probably similar. Inclusion of an assumed 5 kJ mol⁻¹ uncertainty in ΔH for R2 adds a factor of 1.8 uncertainty in k_{-2} . Combined, the total uncertainty (2 σ) in the absolute rate constant for k_{-2} is estimated as a factor of about 2.5. Assuming the uncertainty in the measured cracking pattern of cyclopentyl ($\gamma_1 \approx k_3/k_{-2}$) at 1050 K is small, which we presently believe, the uncertainty in the ring opening rate constant k_3 is similar to that for k_{-2} at this temperature. The extrapolation to higher or lower temperatures is less certain because the experimental data can be fit well with alternative models employing a range of barriers. For comparison, near 1000 K our k_3 is about 30 % smaller than computed by Sirjean et al.,⁷ and 15 % larger than estimated by Wang et al.,¹⁶ differences that are well within our estimated uncertainty. It is, however, 9x larger than derived by Handford-Styring and Walker⁴³ at (673 to 783) K from a kinetic analysis of product formation in a system of slowly oxidizing cyclopentane. This disparity is larger than can be explained by errors of extrapolation. We think it is probably due to uncertainties in the complex analysis needed to extract rate constants in their system.

The temperature dependence of product formation is sensitive to the barriers used for k_{-2} and k_3 . These are in turn sensitive to the barrier for beta scission of allyl (k_4), which has not been measured, and the ring closure rate constants (k_{-3}) needed to fit the data of Tsang and Walker,⁵¹ which show the formation of about 5 % cyclopentene from pent-4-en-1-yl between 1010 K and 1190 K. Under our experimental conditions, the sensitivity coefficients for ethene formation are dominated by k_2 , k_3 and k_{-2} . The present PES leads to a barrier for beta scission of allyl that is approximately 4 kJ mol⁻¹ larger than in the 2011 model; this reduces k_4 and compensates for a smaller k_{-3} (ring closure), thus allowing pent-4-en-1-yl to still form a small amount of cyclopentene as required by the Tsang and Walker⁵¹ experiments. A similar result could be obtained by lowering the pre-exponential factor of R4, but a larger barrier is in better accord with theoretical values.⁹ At 1000 K, our rate constant for ring closure (k_{-3}) is 3x to 7x larger than values estimated by Wang et al.^{16,42} (Table 2). In our model the use of a smaller value of k_{-3} would require a corresponding reduction in k_4 (beta scission of allyl) in order to fit the Tsang and

Walker data. Although our rate constant fits given in Table 2 span 300 K to 2000 K, only k_2 has been unambiguously determined by direct experiments over an extended temperature range.



Figure 3. Branching in cyclopentyl decomposition. The symbols and dotted line show ethene/cyclopentene product ratios (γ , left axis) from experiment and our model, 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 (Section 3.3 of text). Product ratios of Gordon⁶ and Gunning and Stock⁵ are plotted only at their higher temperatures where they relate to k_3/k_2 . The Gunning and Stock values are corrected for cyclopentene formed by disproportionation of cyclopentyl based on $k_{disprop}/k_{recomb.} = 1$ as reported in that work. Indicated uncertainties (2 σ) in 1965GOR⁶ and 1965GS⁵ were estimated by us as 25 %. References: 2006Tsa,¹⁰ 2008SGR,⁷ 2011ABT,⁹ 2015WVDa,¹⁶ 2017ATT,¹⁷ TW = this work (current model at 300 kPa).

3.5 Comparison with current models of cyclopentane combustion. Al Rashidi *et al.*¹⁷ have recently reported an experimental and modeling study of cyclopentane combustion between 740 K and 1250 K, fuel equivalence ratios (ϕ) of 0.5 to 3.0, and pressures of 10.1 bar (10 atm). Reactivity begins at about 800 K, but the rate at a given temperature decreases as the mixtures become richer in fuel. Under sufficiently rich conditions they observe periods of inhibition where the reactivity of a given mixture decreases with increasing temperature. For $\phi = 2$ and $\phi = 3$ this

occurs at temperatures roughly in the range of 860 K to 980 K. Their proposed kinetic model was sensitive to absolute and relative rate constants for beta C-H and C-C scission (k_{-2} and k_3) in cyclopentyl radical and required k_3/k_{-2} branching ratios different from our previously measured values⁹ to reproduce both the low temperature reactivity and the observed inhibition. Figure 3 summarizes data related to the branching ratio k_3/k_{-2} . Lines therein show values of k_3/k_{-2} from various sources and are high pressure limits unless otherwise denoted. Individual points indicate experimentally measured values of the branching (γ) between the ethene and cyclopentene products. Because of the slight reversibility of ring opening, these are not strictly identical to k_3/k_{-2} , but all current models suggest the difference is minimal, far smaller than indicated differences in k_3/k_{-2} . Note that extrapolation of the experimental γ values to high pressure limits would slightly increase differences with the k_3/k_{-2} values.

Figure 3 shows that the theoretically derived branching ratios, and those used in the model of Al Rashidi *et al.*, are significantly smaller than values derived from measured product ratios. They are also smaller than the lower limit of 1.5, which we have argued (Section 3.3) is necessary to maintain a reasonable consistency in relative rates of H atom addition to olefins. 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 Gordon⁶ and Gunning and Stock⁵ 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.

It is possibly significant that the kinetics model of Al Rashidi *et al.* does not contain disproportionation reactions of cyclopentyl, reactions which provide additional routes to cyclopentene and in that respect mimic smaller values of k_3/k_{-2} . Such chemistry would tend to terminate radical chains, possibly leading to inhibition under fuel-rich conditions. It would also potentially lead to increased low temperature reactivity at smaller fuel equivalence ratios because of the enhanced reactivity of the double bond and allylic hydrogens of CPE compared with the

 sp^3 hydrogens of cyclopentane. Uncertainties in the rate constants for the formation of ringopened dienes (Figure A4 of the Appendix) and the subsequent chemistry of these compounds represent another area of ambiguity. A detailed investigation of whether these issues can explain the apparent disagreement between measured branching ratios and values deduced from global reactivity studies is a topic for future work.

4. SUMMARY AND CONCLUSIONS

We have investigated the addition of H atoms to cyclopentene at temperatures of (863 to 1167) K and pressures of (160 to 370) kPa using shock tube methods. Addition of H to the double bond leads to a cyclopentyl radical that rapidly ring opens and decomposes to ethene and allyl radical. Rate constants for this process have been determined and related to the high pressure limiting rate constant for H atom addition. These data are combined with a TST model and literature results at lower temperatures to develop a recommended rate expression covering 300 K to 2000 K. The data allow the relative and absolute rates of C-C and C-H scission in cyclopentyl radical to be deduced. Near 1000 K, ratios of C-C to C-H scission less 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 derived in previous work.⁹ Results are compared with recent theoretical studies and detailed kinetic models of cyclopentyl are in qualitative agreement, but there remain discrepancies in branching ratios determined by experiment and those found by computation or global reactivity studies.

Supporting Information. Table of experimental product concentrations and shock conditions. Molecular properties and other parameters used in the TST and RRKM calculations. Thermodynamic parameters of the model species in tabular and NASA polynomial format.

APPENDIX: SECONDARY REACTIONS AND CYCLOPENTENE PYROLYSIS

Product Data. The Supporting Information includes data from individual experiments with mixtures A through F. Selected product data for mixtures A (1033 K to 1157 K, HME as H atom precursor) and F (863 K to 1068 K, 2-iodopropane as H precursor) are summarized in Figures A1 and A2. With HME as the H atom source, the main products in order of decreasing concentration are cyclopentadiene, isobutene, ethene, methane, *m*-xylene, 1-(3-butenyl)-3,5-dimethylbenzene, propene, 1,4-pentadiene, *E*-1,3-pentadiene, *Z*-1,3-pentadiene, 1,5-hexadiene, 1-butene, 1,3-butadiene, allene, ethane, and acetylene. Isobutene is from our H atom precursor while the other components are attributed as direct or indirect products of cyclopentene or the 135TMB used as inhibitor and rate reference. Analogous results are obtained for the other mixtures, with some differences depending on the temperature standard and specific H-atom precursors. Cyclohexene is found when chlorocyclohexane is the temperature standard. Experiments using 2-iodopropane as the H-atom source lead to propene via reactions R9 and R11. This system also produces propane at levels up to 1.8 % of propene, undoubtedly due to minor abstraction of H by the propyl radical intermediate:

$$YH + i - C_3H_7 \rightarrow Y + C_3H_8$$
 (YH denotes any H donor) (R14)

This bimolecular process becomes relatively less important at higher temperatures where it cannot compete with unimolecular decomposition of isopropyl (R11). Trace iodocompounds, consistent with recombination of radicals with iodine atoms were also noted in this system but not quantitated. When $tBPO/H_2$ is used to generate H via R7, R8, we find the expected methane and acetone, as well as substantial quantities of ethane. The high concentration of ethane reflects that self-recombination of methyl is comparable in rate with competing H abstractions from H₂ (R8), cyclopentene, and the 135TMB inhibitor.

The above compounds constitute all components identified at levels approximately 1 % or greater of the ethene product, which is the main stable olefin expected from the breakdown of cyclopentene induced by addition of H (Scheme 1). The high sensitivity of GC/MS allowed tentative identification of some other species present at still lower levels. These were either minor impurities in the starting mixture or species expected from the chemistry of trace radicals; we do not believe they affect our analysis or conclusions.



Figure A1. Distribution of selected products from mixture A. Results for other mixtures are qualitatively similar. cPDE = cyclopentadiene, (allyl+DMB) = the recombination product of allyl radical with 1,3-dimethylbenzyl (DMB), 1,5-HDE = 1,5-hexadiene; 1,4-PDE = 1,4-pentadiene, 1,3-BDE = 1,3-butadiene.



Figure A2. Distribution of selected products from mixture F. cPDE = cyclopentadiene, (allyl+DMB) = the recombination product of allyl radical with 1,3-dimethylbenzyl (DMB), 1,5-HDE = 1,5-hexadiene; 1,4-PDE = 1,4-pentadiene, 1,3-BDE = 1,3-butadiene, E13PDE = (E)-1,3-pentadiene.



Figure A3. Unimolecular rate constants for CPE \rightarrow cyclopentadiene + H₂. Solid line shows the shock tube pyrolysis result of Lewis et al.⁵² (dashed line is an extrapolation); experimental points are values from present experiments assuming a unimolecular mechanism. Radical processes are inferred to be important at the lower temperatures of our study.



Figure A4. Unimolecular rate constants relevant to formation of pentadienes (PDE) from cyclopentene (CPE). 14PDE = 1,4-pentadiene; 13PDE = 1,3-pentadiene (sum of *E* and Z isomers). Filled and open markers are experimental points from the respective high and low temperature data sets assuming a unimolecular mechanism. Dashed lines show $k(CPE \rightarrow 13PDE)$ and $k(CPE \rightarrow 14PDE)$ used in the kinetic model of AI Rashidi *et al.*¹⁷; the dotted line is $k(CPE \rightarrow 12PDE)$ from Herzler et al.⁵³; heavy solid line is k(1-pentene \rightarrow allyl + C₂H₅) from Tsang.⁵⁴

Reactions of Secondary Radicals. Attack of H atoms on 135TMB via R12 and R13 introduces 3,5-dimethylbenzyl radicals (DMB) and methyl radicals into the system; addition of H to CPE and the ensuing decomposition of cyclopentyl leads to formation of allyl radicals (R1). These three secondary radicals are unreactive compared with H atoms and are expected to adopt relatively high concentrations in the shocked gas. Methyl is more reactive than the resonance stabilized allyl and DMB radicals and can form methane by abstraction of H from closed shell species, primarily 135TMB or CPE, which are the only hydrocarbons present in large concentrations.

$$CH_3 \bullet + 135TMB \rightarrow CH_4 + 3,5$$
-dimethylbenzyl \bullet (DMB) (R15)

$$CH_3 \bullet + CPE \rightarrow CH_4 + cC_5H_7 \bullet (cyclopentenyl)$$
 (R16)

It can also recombine with the other prevalent radicals in the system:

$$CH_3 \bullet + DMB \rightarrow 3,5$$
-dimethylethylbenzene (R17)

$$CH_3 \bullet + allyl \bullet \rightarrow 1$$
-butene (R18)

$$CH_3 \bullet + CH_3 \bullet \rightarrow \text{ethane}$$
 (R19)

Allyl radicals from R1 lead to stable secondary products via a variety of reactions, including decomposition, recombination with other radicals, and H transfer reactions:

$$allyl \bullet \rightarrow H \bullet + allene$$
 (R20)

$$allyl \bullet + allyl \bullet \rightarrow 1,5$$
-hexadiene (15HDE) (R21)

allyl• + DMB
$$\rightarrow$$
 1-(3-butenyl)-3,5-dimethylbenzene (R22)

$$allyl \bullet + H \bullet \rightarrow propene$$
 (R23)

allyl• + H-CC•
$$\rightarrow$$
 C=C + propene (disproportionation; H-CC• is an unspecified H donor) (R24)

allyl• + RH
$$\rightarrow$$
 propene + R• (RH/R• denotes an unspecified hydrocarbon/radical) (R25)

The above products, methane, ethane, allene, propene, and the various recombination products are all observed (see Figures A1 and A2 and product Table S1). We did not locate the $C_{18}H_{22}$ self-recombination product of DMB, but we expect that it is too large to elute from our GC columns. Mass balances of species such as methyl and allyl are only approximate due to the

complexity of the chemistry; nonetheless the product amounts are consistent with expectations. For example, in experiments with HME, summing the presumed allyl radical products 1,5hexadiene, 1-(3-butenyl)-3,5-dimethylbenzene, 1-butene, allene, and propene consistently yields allyl recovery rates of (85 to 90) % based on ethene amounts. This provides strong support for the mechanism and validity of the kinetic analysis.

Pyrolysis chemistry of cyclopentene. Our main experimental focus is on the kinetics of H atom addition to cyclopentene. Cyclopentene is present in large excess, however, and is just beginning to thermally decompose under our conditions. Previous investigators of CPE pyrolysis have reported some minor products we observe, most notably cyclopentadiene, but also including smaller quantities of pentadienes and 1,3-butadiene. Molecular elimination of H₂ from CPE is a well-studied reaction, but the sources of the other products have not been clearly identified in the literature. Some discussion is provided below. We believe this chemistry has no significant impact on the H atom kinetics, but it could be important in developing detailed kinetic models of the pyrolysis and combustion of C₅ ring structures.

Cyclopentadiene. At high temperatures cyclopentene is well-known to undergo direct molecular elimination of H_2 to give cyclopentadiene.

cyclopentene
$$\rightarrow$$
 cyclopentadiene + H₂ (R26)

The kinetics of R26 were reported by Vanas and Walters⁵⁵ in 1948 and the reaction has since been studied experimentally by a number of researchers.^{4,52,56-61} Lewis *et al.*⁵² determined rate parameters between 1020 K and 1190 K using a comparative rate shock tube technique similar to ours and later⁶¹ showed these to be consistent with static studies near 700 K. Their parameters suggest only about a 5 % loss of CPE via R26 even at our highest temperatures. Unimolecular rate constants for cyclopentadiene formation derived from our experiments are shown in Figure A3, with rate parameters collected in Table A1. The present experiments used relatively large concentrations of CPE and relatively small scavenger/CPE ratios, conditions that are not ideal for isolating the unimolecular reaction; nonetheless, the rate constants obtained at the upper end of our temperature range are within 5 % of those of Lewis *et al.* An additional route is necessary, however, to explain its formation at our lower temperatures, where the molecular reaction is

		-			
Reaction ^a	<i>k</i> / s ⁻¹	Temp. (K)	Pres. (kPa)	Method	Ref.
$\text{CPE} \rightarrow \text{cPDE} + \text{H}_2$	2.24x10 ¹³ exp(-30193/T)	1020-1189	≈ 100	ST-CR ^{b,c}	1974Lew ⁵²
	2.24x10 ¹³ exp(-30193/T)	700-1200	NS d	Review	1984Lew ⁶¹
	6.34x10 ¹² exp(-28360/T)	1070-1170	≈ 340	ST-CR ^{b,e}	This Work
$CPE \rightarrow 14PDE$	1.36x10 ¹⁶ exp(-40980/T) ^{f,g}	1038-1167	≈ 340	ST-CR ^{b,c}	This Work
	4.0x10 ⁷ exp(-20490/T) ^h	863-1068	≈ 220	ST-CR ^{b,c}	This Work
	5.04x10 ¹⁵ exp(-48737/T)	740-1250	1000	Estimate ⁱ	2017ATT ¹⁷
$CPE \rightarrow 13PDE$	4.9x10 ¹¹ exp(-29565/T ^h	863-1068	≈ 220	ST-CR ^{b,c}	This Work
	5.06x10 ¹⁵ exp(-33213/T)	740-1250	1000	Estimate ⁱ	2017ATT ¹⁷
1-pentene \rightarrow allyl + ethyl	1.0x10 ¹⁶ exp(-35900/T)	1010-1160	170-520	ST-CR ^{b,j}	1978Tsa ⁵⁴

Table A1. Summary of kinetic data relevant to decomposition of cyclopentene (CPE).

^a CPE = cyclopentene; cPDE = cyclopentadiene; 14PDE = 1,4-pentadiene; 13PDE = 1,3-pentadiene ^b Shock Tube-Comparative Rate ^c *t*-butanol standard ^d Not stated; ^e hexamethylethane standard ^f Mixtures A to D ^g tentatively assigned to a unimolecular process ^h Mixture F; descriptive parameters valid for this study only; mechanism is uncertain and may include significant radical contributions; ⁱ Used in kinetic model of cyclopentane oxidation ^j cyclohexene standard.

slow. We presume the source to be abstraction of H from cyclopentene followed by subsequent beta C-H scission or disproportionation reactions of cyclopentenyl radicals (cC_5H_7):

 $X \bullet + \text{cyclopentene} (cC_5H_8) \rightarrow XH + cC_5H_7 \bullet (X \bullet \text{ is any active radical})$ (R27)

$$cC_5H_7 \bullet \rightarrow cyclopentadiene (C_5H_6) + H \bullet$$
 (R28)

$$R \bullet + cC_5H_7 \bullet \rightarrow cyclopentadiene (C_5H_6) + RH$$
 (disproportionation) (R29)

Abstraction R27 gives two isomeric cyclic C_5H_7 species, both of which can lead to cyclopentadiene. Our previous experimental and modeling work with HME/hydrocarbon mixtures²¹ indicates that H atoms are the main abstracting radical (X•) under our conditions, but CH₃ and other less reactive alkyl radicals may also play a role. We did not observe recombination products of cyclopentenyl (cC_5H_7 •) in the product spectrum, suggesting that it rapidly decomposes via R28 to cyclopentadiene and H in the present experiments.

Pentadienes. Lewis and co-workers^{61,62} mentioned the formation of small amounts of pentadiene (unspecified isomers) in their shock tube studies of CPE pyrolysis, but provided no quantitative details or explanation for its formation. Herbinet *et al.*⁴ reported in 2016 the formation of both 1,3-pentadiene and 1,4-pentadiene in Jet Stirred Reactor (JSR) studies of CPE pyrolysis at temperatures of 773 K to 1073 K, but likewise did not propose chemical pathways. We find 1,4-pentadiene (14PDE) at levels ranging from <1 % to about 6 % of cyclopentadiene, with the

relative importance increasing with temperature. We find a similar amount of 1,3-pentadiene (13PDE), including both *E* and *Z* isomers. Because of background impurities, 13PDE could be quantified only for Mixture F, which used a more purified sample of cyclopentene. Even for this mixture the *Z* isomer peak exhibited overlap with cyclopentadiene and values were extracted from the mass spectral data, which are generally less precise than FID results. The *E* isomer was favored with an *E/Z* ratio of about 1.6, typical for equilibrated alkenes. Regarding other C₅H₈ isomers, in our previous shock tube study of 1,2-pentadiene (12PDE) pyrolysis⁵³ we found cyclopentene as one of the products and through detailed balance were able to derive *k*(CPE \rightarrow 12PDE) = 4.8x10¹⁴ exp(-40950 K/T) s⁻¹. These parameters predict formation of 12PDE in amounts that are near our detection limits; in some experiments at higher temperatures we found a trace peak at the location corresponding to that of an authentic sample of 12PDE, but it is at most a trace product. No other C₅H₈ isomers were identified.

We have derived rate constants for conversion of CPE to 14PDE and 13PDE assuming the processes are unimolecular isomerizations of CPE. The resulting rate parameters are collected in **Table A1** and compared with some literature results in **Figure A4**. Rate constants for formation of 14PDE are similar for all mixtures at temperatures greater than \approx 1020 K and are tentatively assigned to a unimolecular process. When extrapolated, however, these values increasingly diverge from rate constants obtained at lower temperatures with Mixture F. This suggests a change in mechanism and the presence of secondary pathways at the lower temperatures. Al Rashidi *et al.*¹⁷ have listed parameters for CPE \rightarrow 14PDE and CPE \rightarrow 13PDE in their detailed kinetic model of cyclopentane oxidation. It is a minor process in their model; nonetheless, our data require rate constants that are orders of magnitude different from those they have used. We are uncertain of the origin of their rate parameters; they seem to be attributed to Tsang,⁵⁴ but we could not locate those reactions in the cited article.

Isomerization of CPE to 13PDE or 14PDE requires ring-opening and a hydrogen shift reaction. Although these can be formally written as one-step reactions R30 and R31, the transition states

$$(R30)$$

$$(R31)$$

are convoluted and the energetics are unknown. There exist several experimental^{53,63,64} and theoretical⁶⁵⁻⁶⁷ investigations of isomerizations on the C_5H_8 potential surface, but these have focused on the scrambling of H/D in intramolecular H transfers⁵⁷ or on the reverse formation of cyclopentene from isomeric three and four-membered ring compounds. We are unaware of any investigations of routes to pentadienes using high level computations. An alternative to the direct processes involves isomerization of the ring-opened biradical of cyclopentene:

cyclopentene
$$\rightleftharpoons \cdot CH_2$$
-CH=CH-CH₂-CH₂• (R32)

•CH₂-CH=CH-CH₂-CH₂•
$$\rightarrow$$
 CH₂=CH-CH₂-CH=CH₂ (R33)

•CH₂-CH=CH-CH₂-CH₂•
$$\rightarrow$$
 (*E*/Z) CH₂=CH-CH=CH₂-CH₃ (R34)

For this mechanism, the observed high-pressure limiting rate constant for 14PDE would be

$$k_{14\text{PDE}} = \frac{k_{33}k_{32}}{(k_{-32} + k_{33})}$$

Without additional information it is not possible to assign unambiguous rate constants, particularly since R33 (and R34 for formation of 13PDE) could involve multiple steps. Ring opening (R32) involves breaking an allylic C-C bond and rate constants should be similar to those reported by Tsang⁵⁴ for fission of the allylic C-C bond in 1-pentene. As shown in Figure A4, these are much larger than our experimental values for pentadiene formation. This is consistent with the absence of any obvious facile routes to pentadienes or other products from the biradical, so reclosure of the ring is the dominant expected path. We speculate that there may be alternative minor routes involving H transfers and possibly carbene intermediates. Similar ideas have been advanced to explain the allene \leftrightarrow propyne isomerization,⁶⁸⁻⁷¹ the pyrolysis of 1,3-butadiene,⁷² and products observed in the thermal decomposition of 1,2-pentadiene.⁵³ The kinetics of such reactions are not well understood at present, but we suggest that this type of chemistry may well be a common complication in polyene systems. An alternative, or possibly additional source of pentadienes, involves abstraction of H from cyclopentene, followed by reversible ring-opening to a linear C₅H₇ radical and subsequent attachment of H via abstraction or disproportionation reactions. Such an additional mechanism might be a plausible route at lower temperatures, where unimolecular processes are slower and radical intermediates have relatively long lifetimes.

Whatever the process or processes, pentadienes are minor products of CPE decomposition under our conditions. If one extrapolates the kinetic parameters obtained at higher temperatures for 14PDE (Figure A4 and Table A1), formation of 14PDE and cyclopentadiene would become equally important at about 1600 K. Further investigation of pathways to 14PDE and 13PDE might therefore be necessary to understand the behavior of cyclopentene at high temperatures. Theoretical investigations would be of value. In any case pentadiene formation appears to be unrelated to H addition to CPE.

1,3-Butadiene. We find low levels of 1,3-butadiene (13BDE) in all mixtures. Lewis and coworkers^{61,73} and Herbinet *et al.*⁴ also noted small amounts in their respective shock tube and JSR studies of CPE pyrolysis, and it is found by Al Rashidi *et al.*¹⁷ in JSR studies of cyclopentane oxidation. As with the pentadienes, the mechanism of formation is unknown. The overall reaction corresponds to ring opening and loss of CH₂ from CPE. The unimolecular process would have an insurmountably high barrier, suggesting a radical pathway. One alternative is isomerization of the ring-opened isomer of cyclopentyl, pent-4-en-1-yl, to either pent-1-en-3-yl or pent-1-en-4-yl, species which would rapidly decompose to methyl and 13BDE.¹⁰ Herbinet et al.⁴ have adopted this mechanism in their 2016 model of CPE pyrolysis. However, in our previous study⁹ of the decomposition of thermally-generated cyclopentyl radicals, which proceeds through pent-4-en-1-yl, 1,3-butadiene was a barely detectable product (<0.4 % of ethene). We have presently confirmed this result in a few ancillary experiments with cyclopentane/2-iodopropane mixtures at temperatures and pressures near 1000 K and 180 kPa, generating cyclopentyl from H + cyclopentane. 13BDE product amounts were <0.5 % of ethene in these experiments, indicating that intramolecular H transfer in pent-4-en-1-yl is slow relative to beta scission of the allyl group (R4), at least when starting with thermalized cyclopentyl radicals. To investigate the possible impact of chemical activation, an RRKM model was

developed using expected isomerization energies near 150 kJ mol⁻¹ as suggested by Hayes and Burgess⁷⁴ or as low as 136 kJ mol⁻¹ based on the computations of Wang et al.¹⁶ Negligible quantities of 13BDE are predicted, implying an alternate route must be operative.

One possibility involves recombination of the biradical formed in R32 with other radicals in the system followed by a facile beta C-C scission to give 1,3-butadiene and a corresponding daughter radical. An alternative involves addition of alkyl radicals such as methyl to the double bond of cyclopentene followed by isomerization and beta C-C scission. Further exploration of the above postulated chemistry would require detailed modeling and is beyond the scope of our study. Our data and analysis suggest, however, that the mechanism of Herbinet *et al.* should be reconsidered. In the context of the current work, the main conclusion is that under our conditions 13BDE is not a significant product of H addition to cyclopentene.

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18. Disclaimer Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation of endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment is necessarily the best available for the purpose.

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