The calculated values of $k_H/k_D$ are plotted in Figure 4. Curve B corresponds to the parameters found from the BEBO calculations described above. Variation of $F_{12}$ above and below the value $3.25 \times 10^5$ dyn cm$^{-1}$ (while keeping $F_{11} = F_{22}$ constant) had little effect on $\nu_s$, but a rather strong effect on $\nu_a$, and hence on $\Gamma$. For $F_{12} = 2.68 \times 10^5$ dyn cm$^{-1}$, very little tunneling is predicted for either reaction.

It does not seem possible, using a transition state theory model, to account for the apparent increase in $k_H/k_D$ with temperature found experimentally. The assumption of tunneling accentuates the apparent discrepancy in the slopes. However, the magnitude of $k_H/k_D$ found experimentally can best be explained, at least within the framework of transition state theory, if tunneling is assumed to occur.

The difference in the Arrhenius activation energies of the two reactions was calculated from the relation

$$(E_A)_H - (E_A)_D = -R\mathrm{d}\ln(k_H/k_D)/\mathrm{d}(1/T) \qquad (15)$$

The values were quite sensitive to the force constants assumed, and particularly to $F_{12}$, and hence the frequency of the asymmetric vibration. They varied from 0.3 kcal mole$^{-1}$ for $F_{12} = 2.68 \times 10^5$ dyn cm$^{-1}$ to $-0.9$ kcal mole$^{-1}$ for $F_{12} = 3.25 \times 10^5$ dyn cm$^{-1}$, which can be compared to the observed value of 0.8 ± 0.7.

# Kinetics of the Thermal Decomposition of 1-Methylcyclopentene[1]

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**Abstract:** The thermal decomposition of 1-methylcyclopentene has been investigated over the temperature region 470–512° and a pressure range of 5–18 mm. The major products in the early stages of the pyrolysis were hydrogen and methylcyclopentadiene isomers. Other products found in small amounts were ethene, 2-methylpropene, methane, cyclopentene, cyclopentadiene, and 3-methylcyclopentene. The rate of pressure increase followed closely, but not exactly, the behavior of a first-order reaction. The reaction did not appear to be affected by the addition of propene or nitric oxide, or an increase in the surface to volume ratio by a factor of 7. The quantitative results indicated that in the initial portion of the pyrolysis the rate of disappearance of 1-methylcyclopentene was about equal to the rate of pressure increase. The first-order constant for the rate of pressure increase can be expressed as $k = (2.64 \pm 0.12) \times 10^{13} \exp(-60{,}000/RT)$ sec$^{-1}$. Approximately 90% of the pressure increase was due to hydrogen and methylcyclopentadiene, with a slightly greater amount of methylcyclopentadiene.

Thermal gas-phase reactions where a molecular detachment of hydrogen appears to be the predominant process have been receiving attention recently. Cyclopentene,[3] 2,5-dihydrofuran[4a] and its 2-methyl derivative,[4b] and 1,4-cyclohexadiene[5a–c] and its 1-methyl[5d] and 3-methyl[5e] derivatives undergo dehydrogenation as the major, if not sole, reaction. As a part of a continuing investigation in this laboratory of this type of reaction, a study of the kinetics of the thermal decomposition of 1-methylcyclopentene was undertaken.

## Experimental Section

Materials. 1-Methylcyclopentene was purchased from the Aldrich Chemical Co. and was purified further by gas chromatography. Subsequent analysis using a Perkin–Elmer 154D chromatograph with a Golay "R" column showed that the purified compound had a purity greater than 99.9%. The mass spectrum and gas-phase infrared spectrum of the purified sample were in good agreement with the corresponding spectra (liquid phase for the infrared spectra) previously reported.[6] A mixture of the methylcyclopentadiene isomers was prepared by cracking the dimer (Aldrich Chemical Co.) over glass helicies followed by redistillation with further purification by gas chromatography. The retention times of the 1- and 2-methylcyclopentadiene from the unpurified mixture (relative to cyclopentadiene) were in good agreement with previous reports with a dimethylsulfolane column.[7] Also the relative ratio of 1-methylcyclopentadiene to 2-methylcyclopentadiene for an unpurified mixture was 0.82, in satisfactory agreement with prior values. The ultraviolet spectrum (made with a Beckman DU spectrophotometer) in Mallinckrodt SpectrAR $n$-heptane of purified methylcyclopentadienes exhibited a maximum at 248 m$\mu$, which agrees with the results of Mironov and coworkers.[8]

Matheson Co. 2-methylpropene and K & K Laboratories 3-methylcyclopentene were purified by gas chromatography. Cyclopentene, purchased from the National Bureau of Standards with a stated purity of 99.97%, was used after outgassing. Cyclopentadiene, which had been prepared from Kodak technical grade dicyclopentadiene, was provided by D. Knecht of this laboratory. Deuterated cyclopentadiene supplied by Merck Sharp and Dohme of Canada was used without further purification. The amounts of the various deuterated isomers (analysis provided by the supplier) were: cyclopentene-$d_8$ 72.43%, cyclopentene-$d_7$ 23.32%,

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[1] This work was supported in part by a grant from the National Science Foundation.

[2] Abstracted in part from the Ph.D. Thesis of N. H. Turner, University of Rochester, 1968.

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[7] (a) S. M. Csicsery, *J. Org. Chem.*, **25**, 518 (1960); (b) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2312, 2329 (1965).

[8] V. A. Mironov, E. V. Sobolov, and A. N. Elizarova, *ibid.*, **19**, 1939 (1963).

**Table I.** The Amounts of the Various Products of the Thermal Decomposition of 1-Methylcyclopentene (Expressed in (mm cc deg$^{-1}$) × $10^2$)

| $P_0$,$^a$ mm | $\Delta P/P_0$, % | $T$, °C | $C_6H_8$$^b$ | $H_2$ | $C_2H_4$ | $C_4H_8$$^c$ | $CH_4$ | $C_5H_8$$^d$ | $C_5H_6$$^e$ | 3C$_6$-H$_{10}$$^f$ | U$^g$ | $C_6H_{10}$$^h$ | $C_6H_{10}$$^i$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 9.33 | 14 | 470.1 | 55.0 | 50.9 | 2.8 | 2.6 | 1.4 | 0.5 | 0.3 | 0.1 | 0.2 | 405.8 | 347.7 |
| 10.26 | 13 | 469.8 | 54.4 | 52.7 | 3.1 | 2.7 | 1.5 | 0.5 | 0.3 | 0.2 | | 451.0 | 394.6 |
| 9.42 | 17 | 499.9 | 64.3 | 60.1 | 4.9 | 4.1 | 2.5 | 0.9 | 0.8 | 0.1 | 0.4 | 397.1 | 326.1 |
| 9.01 | 25 | 469.3 | 90.3 | 88.5 | 6.6 | 5.5 | 3.8 | 1.2 | 1.9 | 0.6 | 0.9 | 390.6 | 288.3 |
| 10.77 | 25 | 469.4 | 108.5 | 103.6 | 8.1 | 7.1 | 4.8 | 1.5 | 2.3 | 0.8 | 1.8 | 466.9 | 347.0 |
| 9.29 | 27 | 500.1 | 97.8 | 92.9 | 9.7 | 7.8 | 5.6 | 1.7 | 3.0 | 0.2 | 1.6 | 387.8 | 273.5 |
| 9.96 | 30 | 499.9 | 110.1 | 103.9 | 10.5 | 8.8 | 6.2 | 2.0 | 3.7 | 0.3 | 1.4 | 416.4 | 296.7 |
| 11.02 | 25 | 510.1 | 102.0 | 99.7 | 9.2 | 7.9 | 5.5 | 1.4 | 2.4 | 0.1 | 1.7 | 458.1 | 340.4 |
| 5.22 | 23 | 509.3 | 43.5 | 42.5 | 3.6 | 3.2 | 2.1 | 0.6 | 0.9 | | 0.8 | 211.1 | 163.1 |

$^a$ Initial pressure of 1-methylcyclopentene. $^b$ Methylcyclopentadiene. $^c$ 2-Methylpropene. $^d$ Cyclopentene. $^e$ Cyclopentadiene. $^f$ 3-Methylcyclopentene. $^g$ Combined amount of the unidentified compounds. $^h$ Initial amount of 1-methylcyclopentene. $^i$ Final amount of 1-methylcyclopentene.

cyclopentene-$d_6$ 3.66%, and cyclopentene-$d_5$ 0.59%. Matheson Co. nitric oxide was distilled under vacuum from −160 to −196° with end fractions being discarded; just prior to use it was passed through a spiral at −78°. Other compounds used without further purification were hydrogen, Ohio Chemical and Surgical Equipment Co., 99.5%; deuterium, Air Reduction Co., Inc., $D_2$ 92.6%, HD 6.9%, $H_2$ 0.5%; methane, Phillips Petroleum Co., 99.98%; ethene, Phillips Petroleum Co., 99.97%; propene, Phillips Petroleum Co., Research Grade; 1,3-butadiene, Matheson Co., Instrumental; *cis*-2-butene and *trans*-2-butene, Matheson Co., CP; and acetylene, Airco, Industrial.

**Apparatus and Procedure.** The apparatus has been described previously.[4a,9] In the product analysis portion of the system a spiral trap was added in series with the existing trap. The thermocouple was standardized against the melting point of pure zinc (419.5°) and was found to be less than 0.1° in error. After the completion of an experiment the products were separated usually into two fractions, condensables and noncondensables at −196°. The amount of gases noncondensable at −196° was measured in a gas buret. In four experiments the quantity of gases condensable at −196°, but volatile at 25°, was found in an auxiliary, grease-free system, and all of the gases in the reaction vessel at the time the mixture was removed were accounted for by both fractions, 101 ± 1%.

Analysis. Hydrogen and methylcyclopentadiene were found to be the major products of the thermal decomposition of 1-methylcyclopentane. A reaction mixture of products condensable at −196° dissolved in Mallinckrodt SpectrAR *n*-heptane exhibited a maximum absorption at 247 mμ. The gas-phase infrared spectrum of the reaction products condensable at −78° showed strong absorption peaks attributable to methylcyclopentadiene. The mass spectrum of the reaction products, made with an Atlas CH4 mass spectrometer, gave a major peak at *m*/*e* 80 (reduced ionizing voltage), and the intensity of the peak at *m*/*e* 81 was approximately that expected for a compound of the molecular formula $C_6H_8$. The retention times of the major isomers of methylcyclopentene with two columns were essentially identical with the retention times for the major product peaks observed for the condensable products at −196°.

The following minor products, listed in their approximate order of importance, were detected: ethene, 2-methylpropene, methane, cyclopentene, cyclopentadiene, unidentified compounds **1** and **2**, 3-methylcyclopentene, propene, *trans*-2-butene, acetylene, $C_3H_4$, and $C_4H_6$. In most cases the identifications were made with both gas chromatography and mass spectroscopy. *cis*-2-Butene was not observed, since it and 1,3-butadiene had very similar retention times under the chromatographic conditions used. With *trans*-2-butene present, *cis*-2-butene should be expected.[10] Two unidentified compounds (**1** and **2**) had retention times greater than 1-methylcyclopentene and the methylcyclopentadienes (Golay "R"). There were peaks observed mass spectrometrically at *m*/*e* 92 and 94; however, they were not positively ascribed as being unidentified compounds **1** and **2**. In addition, very small peaks were found at *m*/*e* 93, 95, and 96, along with peaks at about 108, 112, and 120. The exact *m*/*e* ratio of the latter group could not be fixed accurately.

A gas chromatographic analysis performed on the noncondensables at −196° indicated the presence of hydrogen and methane. Mass spectrometric analyses of the noncondensable gases at −196° provided quantitative results. The intensities of the peaks at *m*/*e* values of 2, 15, and 16 were measured rapidly and repetitively by variation of the magnetic field. The relative amounts of hydrogen and methane, after depletion corrections, were calculated by the use of sensitivity factors found from standards in the expected region of compositions. The percentage composition was also determined independently from the pressure of the sample. The results from both methods agreed well with each other in most cases.

The fraction condensable at −196° was analyzed quantitatively by gas chromatography (Golay "R" at 50°). Unreacted 1-methylcyclopentene served as the standard for analysis purposes with comparisons made to prepared standards. The unidentified compounds were assumed to have the same sensitivity as 1-methylcyclopentene.

In Table I the combined results from the analyses of both fractions are given. In every experiment there seems to be a slightly larger amount of the methylcyclopentadienes than hydrogen, and this difference is near the magnitude of ethene or 2-methylpropene found, with ethene always being greater. Also, the quantity of methane is about equal to the combined amount of cyclopentene and cyclopentadiene. 3-Methylcyclopentene and the combined amount of the unidentified compounds are generally less than 2% of the hydrogen found. It will also be noted that the relative amount of methylcyclopentadiene isomers and hydrogen decreases as the extent of the reaction and/or temperature increases.

The relationship of the quantities of the major products, hydrogen and methylcyclopentadiene, and the amount of 1-methylcyclopentene disappearing, to the overall change in the number of moles in the system was calculated from the change in the total pressure. Hydrogen was about 89% as large as the pressure change (additional results included) while methylcyclopentadiene was 91%. The $\Delta n$ to Δ(1-methylcyclopentene) ratio was 0.98 ± 0.03, with most of the error due to the fact that Δ(1-methylcyclopentene) was obtained from the chromatographic analysis of a complex mixture. Within the accuracy of the results it appears that the pressure change measured satisfactorily the disappearance of 1-methylcyclopentene under the experimental conditions of this study.

## Results

**Order of Reaction.** The overall rate of pressure increase closely followed first-order kinetics. No inflection points or indications of an induction period appeared in the pressure–time plots. Starting pressures of 1-methylcyclopentene were varied by the following factors: 2.4 at 469°, 3.7 at 491°, and 2.9 at 509°. Calculated first-order rate constants appeared to be independent of the initial pressure in these experiments. The rate constants computed from the time for a 12.5 and 25% pressure increase were not significantly different. The ratio $t_{25}/t_{12.5}$ averaged 2.05 ± 0.01 from 35 experiments. This value is somewhat low compared to the ideal value of 2.15 and may be caused by reactions which the initially formed products undergo. A log $(P_0/(2P_0 - P_t))$ *vs.* time plot showed the points fall-

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(9) C. A. Wellington, *J. Phys. Chem.*, **66**, 1671 (1962).

(10) (a) B. S. Rabinovitch and K. W. Michel, *J. Am. Chem. Soc.*, **81**, 5065 (1959); (b) R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, 57, 1936 (1961).

ing fairly well on straight lines; and the rate constants determined from the slopes agreed well with the rate constants from pressure–time curves, assuming first-order behavior.

**Temperature Dependence.** An Arrhenius plot of log $k$ *vs.* $(1/T)$ for experiments over a temperature range 469.7–512.1° and a pressure range of 8–11.3 mm from the rate of pressure increase, 25%, gave a straight line. The activation energy was found to be 60.0 ± 0.8 kcal/mole. With $E = 60.0$, $A = (2.64 \pm 0.12) \times 10^{13}$ $\text{sec}^{-1}$ was computed. No significant changes were found in $E$ using the rate constant determined from a 12.5% pressure increase. The first-order rate constant can be expressed as

$$k_{25} = (2.64 \pm 0.12) \times 10^{13} \exp(-60{,}000/RT)\ \text{sec}^{-1}$$

Setting $A = \kappa e(kT/h) \exp(\Delta S^*/R)$ with $\kappa$ assumed to be unity, a value of −1.0 gibbs at 490° for $\Delta S^*$ was found. From the quantitative analyses for hydrogen and methylcyclopentadiene, rate expressions for their formation were computed also. There was no appreciable difference in the activation energy compared to the overall decomposition, and the expressions found were

$$k_{\text{H}_2} = (1.79 \pm 0.08) \times 10^{13} \exp(-59{,}600/RT)\ \text{sec}^{-1}$$

$$k_{\text{MCPD}} = (1.52 \pm 0.07) \times 10^{13} \exp(-59{,}300/RT)\ \text{sec}^{-1}$$

**Effect of Surface and Added Gases.** Table II gives the observed rate constants, compared to those calculated from the Arrhenius equation, for an increase of the surface to volume ratio by a factor of 7, and various added gases. The possibility of hydrogen undergoing subsequent reaction was investigated by its addition prior to an experiment. Deuterium was used also, with the possibility of isotopic mixing investigated. As can be seen in Table II, an increase in surface or the addition of the various gases did not alter the rate constants markedly. In the cases of the added nitric oxide and hydrogen, and an increase in surface, the distribution of the products condensable at −196° was very similar to that for the normal decomposition. Also, the hydrogen–methane distribution was similar to the normally observed distribution for the products noncondensable at −196°.

**Table II.** Observed Rates for the Pressure Increase of 1-Methylcyclopentene under Special Conditions

| $P_0$,[a] mm | $T$, °C | Special condition | $k_{25}$,[b] $\text{sec}^{-1}$ | $k_{25}$,[c] $\text{sec}^{-1}$ |
|---|---|---|---|---|
| 12.42 | 489.8 | Packed vessel | 1.77 | 1.70 |
| 9.92 | 489.6 | NO, 0.12 mm | 1.81 | 1.68 |
| 10.20 | 489.8 | Propene, 5.04 mm | 1.80 | 1.70 |
| 7.58 | 490.0 | Propene, 4.16 mm | 1.78 | 1.73 |
| 10.41 | 490.1 | $H_2$, 1.29 mm | 1.80 | 1.75 |
| 11.91 | 489.6 | $D_2$, 1.52 mm | 1.65 | 1.68 |
| 6.21 | 490.0 | $D_2$, 6.90 mm | 1.65 | 1.73 |

[a] Initial pressure of 1-methylcyclopentene. [b] Experimental rate constants have been multiplied by $10^4$. [c] Rate constants multiplied by $10^4$ computed from the Arrhenius expression.

Some HD appeared to have been formed by processes other than the molecular detachment of hydrogen from 1-methylcyclopentene when deuterium was present, but the amount could not be determined. No isotopic addition was found, within experimental error, from low-voltage mass spectral analyses, for methane, ethene, methylcyclopentadiene, and 1-methylcyclopentene, and only a slight increase, 1.2%, for 2-methylpropene.

**Copyrolysis of 1-Methylcyclopentene and Cyclopentene-$d_8$.** At 490° 1-methylcyclopentene and cyclopentene-$d_8$ were decomposed together. Under the experimental conditions the cyclopentene-$d_8$ decomposed to a small extent to give as major products, cyclopentadiene-$d_6$ and $D_2$; and as minor products, ethene-$d_4$ and propene-$d_6$.[3c] The results of the mass spectrometic analyses of the products are given in Table III.

**Table III.** Mass Spectrometric Analyses of Reaction Mixtures from the Copyrolysis of 1-Methylcyclopentene and Cyclopentene-$d_8$ at 490°

| $P_0$,[a] | $P_d$,[b] | Relative ion intensities | | | | | |
|---|---|---|---|---|---|---|---|
| mm | mm | 3/4 | 17/16[e] | 57/56[h] | 58/56[h] | 81/80[h] | 83/82[h] |
| 6.19[c] | 7.84 | 0.230[d] | 0.38[f] | 0.61 | 0.23 | | |
| 6.22[c] | 8.29 | 0.204[d] | 0.44[g] | 0.66 | 0.20 | 0.038 | 0.004 |

[a] Initial pressure of 1-methylcyclopentane. [b] Initial pressure of cyclopentene-$d_8$. [c] Reaction time 33 min, producing 28% decomposition of 1-methylcyclopentene, if alone. [d] A value of 0.139 was obtained for 25% decomposition of cyclopentene-$d_8$ at 500–510° in ref 3c. [e] Average of low voltage and 70-eV spectra. [f] An average value of 0.41 was computed for the deuterium to hydrogen atom abstraction ratio of a methyl radical (ref 11) under these experimental conditions. [g] An average value of 0.44 computed as in footnote *f*. [h] Low-voltage spectra with isotopic abundance correction.

A slightly greater amount of HD was formed than would have been expected from only cyclopentene-$d_8$ decomposition (because of incomplete deuteration). From these data estimates of the importance of atomic processes *vs.* molecular elimination in the formation of hydrogen (and deuterium) were made by considering reactions of the type

$$\text{H}\cdot + \text{RH} \longrightarrow \text{H}_2 + \text{R}\cdot \tag{1}$$

A range of values for this type of reaction was used, and it was found that atomic reactions would not contribute greatly (about 2–7%) in the production of hydrogen. From the 17/16 ratio it appears that deuterium was incorporated into the methane formed, as only a trace of methane would have been observed with cyclopentene-$d_8$.[3c] The values found in these experiments are in good agreement with the calculated results of hydrogen and deuterium abstraction by methyl radicals.[11] In view of the possible errors in the calculated and experimental values, the possibility of some formation of methane by a molecular process cannot be ruled out. Small amounts of more highly deuterated methane were found also. The intensities of the ratios of the peaks at $m/e$ 57/56 and 58/56 indicate an appreciable uptake of deuterium in the 2-methylpropene in these experiments. Also, the 57/56 ratio is higher than the probability estimated for deuterium atom abstraction, relative to hydrogen atom abstraction in a single step.

A large peak was observed at $m/e$ 28, but the peaks at $m/e$ 29 and 30 were so small that an accurate determination of their intensities was difficult. Slightly larger values than those expected from isotopic abundances were found for the 81/80 and 83/82 ratios. Very

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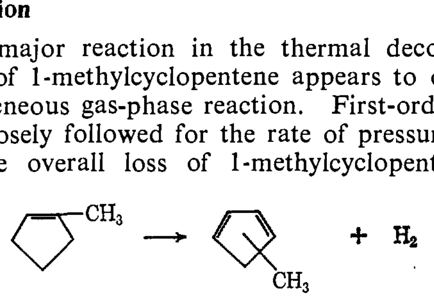
(11) (a) J. G. Larson and A. Kuppermann, Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March 1962, p 24R; (b) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, 33, 31 (1955); (c) S. Toby and K. O. Kutschke, *ibid.*, 37, 672 (1959).

small peaks were noted also in the range $m/e$ 85–100, with the largest peaks being $^1/_{500}$th of the peak intensity of $m/e$ 82.

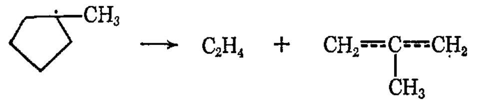
## Discussion

The major reaction in the thermal decomposition (eq 2) of 1-methylcyclopentene appears to occur as a homogeneous gas-phase reaction. First-order kinetics were closely followed for the rate of pressure increase and the overall loss of 1-methylcyclopentene. The ratio of the overall rate of decomposition at 490° of 1-methylcyclopentene compared to that of cyclopentene was 0.93, and methyl substitution caused the activation energy to be 2.3 kcal/mole higher, under conditions most similar to this study.[3c] When only hydrogen production is considered, 1-methylcyclopentene dehydrogenated 0.90 times as fast as cyclopentene. These results are very similar to those found in the 1-methyl-1,4-cyclohexadiene and 1,4-cyclohexadiene dehydrogenations, and it will be noted that these two sets of compounds are very similar structurally.[5a,d] The methylene groups involved in the dehydrogenation could not be identified, owing to the apparent equilibrium of the methylcyclopentadiene isomers.[7b,8]



(2)

From the results with added hydrogen and deuterium a subsequent reaction of hydrogen and 1-methylcyclopentene does not appear to be important, contrary to earlier suggestions for the cyclopentene system.[3b] A methylcyclopentyl radical decomposing to give ethene and a 2-methylpropenyl radical, with a subsequent hydrogen atom abstraction, could account for the approximately equal amounts of ethene and 2-methylpropene. The large amount of deuterium found in the 2-methylpropene in the copyrolysis experiments with cyclopentene-$d_8$ also could be accounted for. The 2-methylpropenyl radical would be expected to have some resonance stabilization, since it is structurally similar to a propenyl radical.[12] A similar reaction to (3) with a cyclopentyl radical to form ethene and a propenyl radical has been suggested from a number of studies.[13]



(3)

Hydrogen atom transfer reactions could account for the methylcyclopentyl radical, and such reactions have been proposed before for other systems.[14] A rapid equilibrium among the isomeric methylcyclopentyl radicals has been indicated by Kallend and coworkers[15] in the pyrolysis of propene from 555 to 640°, as a result of finding an equilibrium mixture of butenes. Such an equilibrium does not seem to be important under the conditions of this study. These investigators also suggested possible reactions of methylcyclopentyl radicals to form cyclopentene and 3-methylcyclopentene. With cyclopentene present cyclopentadiene would be expected under these experimental conditions. Preliminary experiments showed that 3-methylcyclopentene would decompose under the conditions of this study, but its contribution to the observed products would be small.

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[13] (a) A. S. Gordon, *Can. J. Chem.*, **43**, 570 (1965); (b) H. E. Gunning and R. L. Stock, *ibid.*, **42**, 357 (1964); (c) T. F. Palmer and F. P. Lossing, *ibid.*, **43**, 565 (1965).

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[15] A. S. Kallend, J. H. Purnell, and B. C. Shurlock, *Proc. Roy. Soc., Ser. A*, **300**, 120 (1967).