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Thermal Decomposition of Cyclopentene and Cyclopentene-d_8 in the Gas Phase[1]

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Abstract: The thermal decomposition of cyclopentene and cyclopentene-d_8 (72.4% C_5D_8, 23.3% C_5HD_7, 3.7% $C_5H_2D_6$, and 0.6% $C_5H_3D_5$) was studied in the gas phase at 480–530° and 4–34 Torr in a static system. In the initial phases of the pyrolysis, the reaction proceeds mainly by dehydrogenation to form hydrogen and cyclopentadiene, but at greater extents of decomposition the participation of minor reactions forming ethylene and propylene increases. The first order rate constants for dehydrogenation obtained from pressure increase measurements and from hydrogen analysis can be represented for H_2 and D_2 formation, respectively, by $k_{H_2}(\text{sec}^{-1}) = (0.63 \pm 0.01) \times 10^{13} \exp(-57{,}800 \text{ cal mol}^{-1}/RT)$ and $k_{D_2}(\text{sec}^{-1}) = (0.99 \pm 0.02) \times 10^{13} \exp(-60{,}300 \text{ cal mol}^{-1}/RT)$. The analysis of HD/D_2 formed from cyclopentene-d_8 and of H_2/D_2 formed from an equimolar mixture of cyclopentene and cyclopentene-d_8 yields the respective isotope effects $k_{HD}/k_{D_2} = (0.82 \pm 0.01) \exp(1250 \text{ cal mol}^{-1}/RT)$ and $k_{H_2}/k_{D_2} = (0.637 \pm 0.006) \exp(2500 \text{ cal mol}^{-1}/RT)$. In copyrolysis experiments carried to 5% completion in C_5H_8 and 1.7% completion in C_5D_8, the dehydrogenation reaction appears to be mainly the elimination of a molecule of hydrogen with atomic reactions contributing not more than 2% of the total $H_2 + D_2$. The minor product ethylene was formed with negligible isotopic mixing, whereas propylene exhibited a significant degree of isotopic mixing.

Recently, increasing attention has been given to thermal decomposition reactions which proceed by the homogeneous elimination of molecular hydrogen from five- and six-membered unsaturated hydrocarbon or heterocyclic rings to form a molecule with some aromatic character.[3–9] The simplest five-membered ring compound of these, cyclopentene, decomposes near 500° to yield a mixture of which ~95% is hydrogen and cyclopentadiene and ~5% is ethylene and propylene.[3] Rate constants have been reported only for the disappearance of cyclopentene derived from pressure measurements but not for the formation of hydrogen.

Some interesting questions arise concerning the general mechanism of dehydrogenation. Is the process an intramolecular one? What ring positions are involved? The Woodward–Hoffmann symmetry rules predict a concerted elimination of H_2 from the nonadjacent 3,5 positions of 1-cyclopentene.[10] In apparent support of this prediction, dehydrogenation was found to proceed readily in the case of 2,5-dihydrofuran,[5a,11] 3-pyrroline,[6] and 2,5-dihydrothiophene,[7] where the available hydrogens are located only at the 3,5 positions. In the case of cyclopentene, an estimate of ~12 was made for the ratio of 3,5- to 3,4-hydrogen elimination. This determination was based on measurements of the isotopic composition of cyclopentadiene formed at 550° in the decomposition of 4-cyclopentene-d_1 and

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[5] (a) C. A. Wellington and W. D. Walters, *ibid.*, **83**, 4888 (1961); (b) T. L. James and C. A. Wellington, *J. Chem. Soc. A*, 2398 (1968).

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[10] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim, Germany, 1970, pp 143–144.

[11] Prior isomerization of 2,5-dihydrofuran to form 2,3-dihydrofuran which then eliminates hydrogen from adjacent carbon positions can be ruled out since the latter compound is known to react by more complex paths: C. L. Wilson, *J. Amer. Chem. Soc.*, **69**, 3002 (1947).

on the assumption that the isotope effect for eliminating HD *vs.* H_2 could be ignored.[12] In the reverse reaction of the noncatalytic hydrogenation of cyclopentadiene at 300° with D_2 ($\sim$40 atm), the nmr spectrum of the resulting cyclopentene-d_2 revealed only *cis*-3,5-cyclopentene-d_2 being formed.[13]

Only in the investigations of the decomposition of 1-methylcyclopentene[4] and 3-pyrroline[6a] carried out in this laboratory was the molecularity of the elimination directly measured by isotopic techniques. The hydrogenation results at 300° do support a molecular addition of D_2 to cyclopentadiene.[13] However, at the higher temperatures used to study the dehydrogenation of cyclopentene, the presence of concurrent secondary reactions forming ethylene and propylene suggests the need for additional work to investigate the extent of intramolecular hydrogen elimination.

It is important to know the value of the isotope effect for the thermal elimination of H_2, HD, and D_2 in order to properly analyze isotopic studies of dehydrogenation, as in the case of the 4-cyclopentene-d_1 investigation above.[12] In addition to its mechanistic utility, the isotope effect is of interest in its own right, and while previous measurements have not been made, such a primary effect would be expected to be substantial. At 500°, the ratio of rate constants for H relative to D abstraction by CD_3 radicals from alkanes is approximately 3,[14] and the isotope effect for the elimination of HX and DX (X = Br, OAc, and Cl) is near 2.[15] However, the heterolytic nature of the latter reactions precludes direct application of this isotope effect to the homolytic elimination of hydrogen.

Thus an investigation of the thermal decomposition of cyclopentene, cyclopentene-d_8, and mixtures of these compounds was undertaken to study the molecularity and the isotope effect of the dehydrogenation. Additional information concerning the qualitative nature of the secondary reactions forming ethylene and propylene was also obtained.

Experimental Section

Materials and Apparatus. Cyclopentene was obtained from the National Bureau of Standards and was used without further purification. Gas chromatographic and mass spectrometric analyses confirmed the stated purity of 99.996 ± 0.021 mol %, and no *m/e* greater than 69 was found in the mass spectrum. Cyclopentene-d_8 (Merck Sharp and Dohme of Canada, Ltd.) had a stated composition of $\geq$72.4% C_5D_8, $\geq$23.3% C_5HD_7, $\leq$3.7% $C_5H_2D_6$, and $\leq$0.6% $C_5H_3D_5$, which was confirmed by mass spectrometric analyses at reduced electron ionizing voltages. No impurity of molecular weight higher than that which would be expected for c-C_5D_8 was found. Gas chromatographic analysis revealed a chemical purity greater than 99.9%. Cyclopentadiene was prepared and purified from Eastman dicyclopentadiene following the method of Vanas[3a] and was stored at −78° under vacuum. No impurities were found to be present by mass spectrometric and gas chromatographic analysis. Additional compounds which were used as standards and/or addends were obtained from the following sources, all at purities $\geq$99.5%: hydrogen, deuterium (92.6% D_2, 6.9% HD, and 0.5% H_2), and methane (Matheson); deuterium ($\geq$99.65 atom % D) (Bio-Rad); hydrogen deuteride (HD $\geq$98.13%, $H_2 \leq$ 1.87%) (Merck Sharp and Dohme); ethylene and propylene (Phillips). Purities and isotopic compositions were checked using gas chromatography and/or mass spectrometry.

The vacuum system, furnace, and temperature control system were of a conventional type. A Pyrex glass cylindrical reaction vessel (349 ml) was fitted with a thermocouple well extending into its center. The temperature was regulated to ±0.1° and was measured with a platinum, platinum–13% rhodium thermocouple standardized at the melting points of NBS zinc (419.5°) and NBS aluminum (659.7°). The rate of pressure increase during an experiment was determined manometrically to ±0.01 Torr and appropriate dead space corrections were applied. Subsequent to the kinetic experiment the unreacted cyclopentene and products were removed rapidly from the reaction vessel by expansion into a Toepler pump through a series of two cold traps, the coldest of which was at −196°. All the kinetic studies, gas analysis, and sample removal took place in a grease-free environment by using mercury cut-off valves.

Analysis of the Products. The reaction mixture was separated into fractions which were measured on a gas buret. The composition of each fraction was related to its respective volatility at −196° (hydrogen and methane), −96° (ethylene, propylene, and a trace of 1,3-butadiene), and 25° (cyclopentene, cyclopentadiene, and trace products) and was analyzed further using gas chromatography, uv spectroscopy, and mass spectrometry. The total number of moles measured in this way was equivalent to the moles in the reaction vessel, with an average deviation of ±0.4% for reactions carried up to 30% decomposition.

The analysis of isotopic hydrogen required special care. Since a double collector for this mass range was not available on the Atlas CH4 mass spectrometer used in this study, the large difference in depletion rates of H_2, HD, and D_2 from the mass spectrometer sample reservoir had to be taken into account. Repetitive scans of the amu's 2, 3, and 4 were run and the time evolution of the intensity of each peak was plotted. Thus the relative intensity was determined graphically at a preselected time after the start of the analysis. Standard mixtures of similar composition and pressure were frequently analyzed, usually more than one standard analysis for every unknown. In a typical analysis series, the standard deviation in relative sensitivity for H_2/D_2 in a standard mixture was ±0.7% using the above procedure. Some D_2, HD, and H_2 determinations were carried out gas chromatographically at a comparable precision using a 2-m alumina column treated with $MnCl_3$ and operated at −196°.[16] After each isotopic hydrogen was separated on the column, it was oxidized over cupric oxide at 550° and subsequently measured as water vapor on a thermal conductivity detector.

In addition to being analyzed by gas chromatography, the hydrocarbon fractions were analyzed mass spectrometrically for isotopic composition at low ionizing energies. Where standard mixtures of known isotopic composition were not available (*e.g.*, the cyclopentadienes C_5D_6, C_5HD_5, $C_5H_2D_4$, and $C_5H_3D_3$), the relative mass spectrometric response factors were assumed to be the same as those determined for as imilar available mixture (*e.g.*, the cyclopentenes C_5D_8, C_5HD_7, $C_5H_2D_6$, and $C_5H_3D_5$).

Results[17]

The decomposition of C_5H_8 and C_5D_8'[17a] was observed to proceed with a first order rate of pressure increase (ΔP) during the early stages of reaction, and the composition of the major products formed under typical experimental conditions is presented in Table I. Within the accuracy of the analyses, ΔP is equivalent to the pressure of cyclopentene reacted. The amount of hydrogen produced is slightly less than the amount of cyclopentene reacted, and $P_{\text{Hydrogen}}/\Delta P$ does not show any significant temperature or pressure dependence.[17b] For reactions carried to 30% completion, with initial pressures, P_0, near 20 Torr, the average amounts of hydrogen formed relative to ΔP are 0.94 for

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[12] J. E. Baldwin, *Tetrahedron Lett.*, 2953 (1966).

[13] F. A. L. Anet and F. Leyendecker, *J. Amer. Chem. Soc.*, **95**, 156 (1973).

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[16] I. Yasumori and S. Ohno, *Bull. Chem. Soc. Jap.*, **39**, 1302 (1966).

[17] (a) In this and the following discussion C_5D_8' represents the sample of deuterated cyclopentene with composition $\geq$72.4% C_5D_8, $\geq$23.3% C_5HD_7, $\leq$3.7% $C_5H_2D_6$, and $\leq$0.6% $C_5H_3D_5$. In an analogous fashion, a chemical formula followed by a prime is used to represent the sum of isotopically mixed products which have been formed predominantly from either C_5H_8 or C_5H_8', *e.g.*, C_3H_6' and C_3D_6' in Table I. (b) See paragraph at end of paper regarding supplementary material.

Table I. Product Analysis of the Cyclopentene Decomposition

Expt	P_0, Torr[a] C_5H_8	P_0, Torr[a] C_5D_8'	Time, 10^2 sec	Pressure of products in reaction vessel, Torr[a] H_2	HD	D_2	C_5H_6'	C_5D_6'	C_2H_4'	C_2D_4'	C_3H_6'	C_3D_6'
						489°						
H48	22.9		16.9	5.57			5.34		0.35		0.27	
						500°						
HD2	13.2	13.1	1.57	0.53	0.032	0.154	0.62	0.21	0.009	0.009	0.008	0.007
HD5	10.8	10.8	9.58	2.52	0.17	0.78	2.71	0.98	0.095	0.106	0.075	0.081
HD14	3.98	3.98	9.27	0.94	0.055	0.263	0.95	0.34	0.019	0.022	0.016	0.018
HD1	11.7	11.7	26.9	5.86	0.53	2.06	6.11	2.65	0.33	0.42	0.26	0.33
						510°						
D11		21.2	22.9	0.056	0.74	5.10		6.42		0.64		0.37
D12[b]		19.0	23.4	0.23	0.87	4.56	4.26	5.85		1.05		0.63
						520°						
H50	18.7		4.83	5.46			5.54		0.30		0.25	
H51[c]	20.1		4.91	6.04			6.07		0.34		0.27	

[a] See ref 17a for significance of primes. [b] 4.59 Torr of C_5H_6 added. [c] 11.96 Torr of H_2 added.

C_5H_8 and 0.91 for C_5D_8'. No effect on the rate of pressure increase or the product yield is evident with the addition of up to four times as much hydrogen or deuterium as would normally be formed by the reaction. In the early stages of decomposition of an equimolar mixture of C_5H_8 and C_5D_8', the calculated ΔP_H and $\Delta P_D'$ of each component add up to 0.98 ± 0.01 times the measured pressure change.

Pressure Increase Rate Constants. Although small amounts of products are evidently formed from reactions other than a simple first order reaction, the above results validate the use of the overall rate of pressure increase to determine the decomposition rate constants, $k_{\Delta P_H}$ and $k_{\Delta P_D}'$. Rate constants were calculated using the integrated rate equation at 25% decomposition. An Arrhenius plot of the resulting $k_{\Delta P_H}$ and $k_{\Delta P_D}'$ is shown in Figure 1 for experiments with P_0 near 20 Torr.

Molecular Dehydrogenation. The analysis of the hydrogen isotopes formed in the copyrolysis of equimolar C_5H_8 and C_5D_8' mixtures reveals slightly more HD than would be expected from decomposition of C_5D_8' alone (Table I).[18] If it is assumed that only homogeneous metathetical reactions of the type

$$H + R - H \longrightarrow H_2 + R \qquad (1)$$

contribute to this "extra" HD formation, it is possible to calculate an upper limit of 2% of the total (H_2 + D_2) yield as being formed by atomic reactions in copyrolysis experiments carried to 2% decomposition of C_5D_8'. For greater reaction extents of 9 and 25% decomposition of C_5D_8' this value becomes 3 and 5%, respectively.[19]

Thus, most of the hydrogen produced under the above experimental conditions is due to an intramolecular split, and the rate constants k_{H_2} or k_{D_2}' for the respective formation of H_2 or D_2' (D_2 + HD + H_2 from C_5D_8') can be calculated from $P_{\text{Hydrogen}}/\Delta P$ and $k_{\Delta P_H}$ or $k_{\Delta P_D}'$. An nmr analysis of C_5D_8' revealed that in C_5HD_7 (23.3% of the C_5D_8' sample[17a]) H is located with equal probability at each ring position. By also assuming random distribution of H in $C_5H_2D_6$ (3.7% of C_5D_8') and in $C_5H_3D_5$ (0.6% of C_5D_8') and by ignoring secondary isotope effects, it is possible, furthermore, to convert k_{D_2}' to k_{D_2}, the rate constant for D_2 formation. Table II summarizes the Arrhenius parameters of the above rate constants. The values of A_{H_2} and A_{D_2} in Table II are obtained from a least squares analysis using the assigned values of E_{H_2} and E_{D_2} shown in column 3. Assigned values were taken to be those most consistent with the experimental determination of E_{H_2}, E_{D_2}, and the independently determined value of $E_{D_2} - E_{H_2}$.

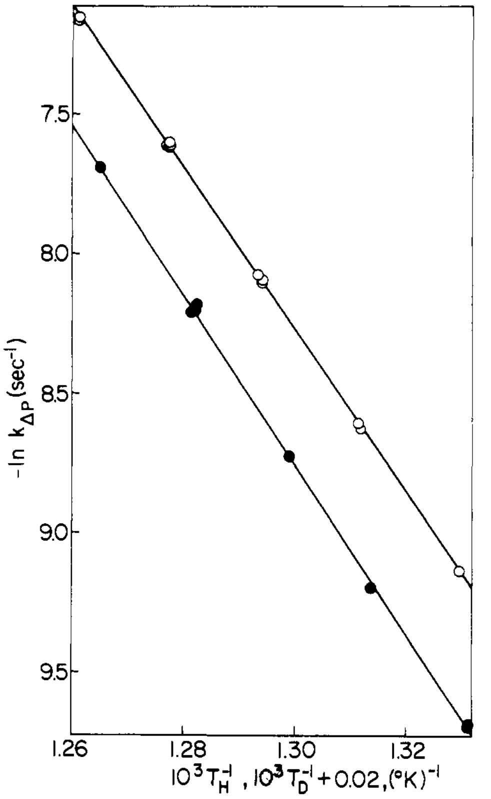

Figure 1. Arrhenius plot of pressure increase rate constants, P_0, near 20 Torr: (○) C_5H_8 and (●) C_5D_8'. Lines represent least squares plots with $E_{\Delta P_H}$ = 57.7 kcal mol^{-1} and $E_{\Delta P_D}'$ = 60.4 kcal mol^{-1}.

The Hydrogen Isotope Effect. A determination of k_{HD}/k_{D_2} (Figure 2) was made using HD/D_2 yields from the C_5D_8' decomposition, and k_{H_2}/k_{D_2} was obtained using H_2/D_2, C_5H_6/C_5D_6', and C_5H_8/C_5D_8' analyses

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[18] The ratio HD/D_2 formed at 500° in C_5D_8' alone at 2, 9, and 25% is 0.156, 0.154, and 0.152, respectively. H_2/D_2 for all the above extents is 0.006.

[19] Wall recombination reactions were not taken into account in determining the "atomic" H_2 formation (reaction 1), as a simple calculation shows that an atom of hydrogen reacts homogeneously with high probability within a 3-mm path of its formation in a typical reaction mixture.

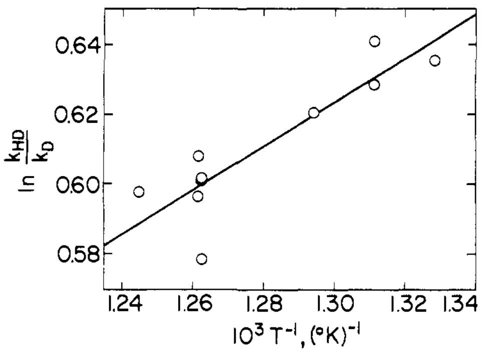

Figure 2. Arrhenius plot of k_{HD}/k_{D_2}. The line represents a least squares plot with $E_{D_2} - E_{HD}$ = 1.25 kcal mol^{-1}.

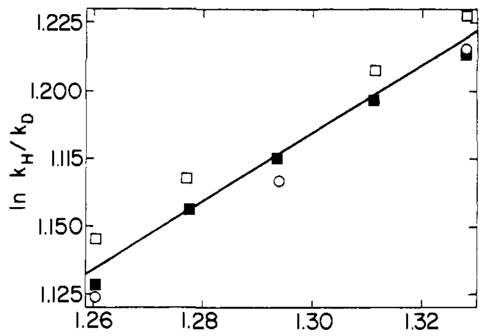

Figure 3. Arrhenius plot of k_{H_2}/k_{D_2}. The symbols distinguish three separate mass spectrometric analysis series. The line represents a least squares plot with $E_{D_2} - E_{H_2}$ = 2.50 kcal mol^{-1}.

Table II. Arrhenius Parameters Determined from Pressure Increase Rate Constants

k^a	E, kcal mol^{-1} b	c	$10^{-13}A$,^{d} sec^{-1}
$k_{\Delta P_H}$	57.7 ± 0.3	57.7	0.63 ± 0.01
$k_{\Delta P_D}'$	60.4 ± 0.6	60.4	1.25 ± 0.02
k_{H_2}	57.7 ± 0.3	57.8	0.63 ± 0.01
k_{D_2}'	60.4 ± 0.6	60.4	1.14 ± 0.02
k_{D_2}	60.5 ± 0.6	60.3	0.99 ± 0.02

[a] Reactions with P_0 near 20 Torr. Rate constant for pressure increase is $k_{\Delta P}$ and for dehydrogenation is k_{H_2} or k_{D_2}; prime denotes the sum of all isotopic species formed from C_5D_8', see ref 17a. [b] Values as determined from least squares analysis include standard deviations. [c] Assigned values which are used in the least squares determination of A, see text. [d] Standard deviations given.

Table III. Arrhenius Parameters for the Isotope Effect

Product analysis[17a]	$E_{D_2} - E_{H_2}$, kcal mol^{-1}	A_{H_2}/A_{D_2}^{a}
$(H_2/D_2)_{2,5\%}$ ^{b}	2.53 ± 0.06	0.637 ± 0.006
$(H_2/D_2)_{9,25\%}$ ^{b}	2.89 ± 0.66	0.65 ± 0.02
$(C_5H_6/C_5D_6')_{9,25\%}$ ^{b,c}	2.04 ± 0.80	0.58 ± 0.01
$(\Delta C_5H_8/\Delta C_5D_8')_{9,25\%}$ ^{b,d}	2.15 ± 1.02	0.57 ± 0.01
$(\Delta P_H, \Delta P_D)$ ^{e}	2.8 ± 0.9	0.63 ± 0.03
(HD/D_2) ^{f}	1.23 ± 0.22^f	0.82 ± 0.01^f

[a] Obtained by least squares analysis with the assigned activation energies: $E_{D_2} - E_{H_2}$ = 2.50 ± 0.0, and $E_{D_2} - E_{HD}$ = 1.25 ± 0.0. [b] Percentages indicate decomposition of C_5D_8' and C_5H_8, respectively. [c] Cyclopentadiene analysis. [d] Cyclopentene reacted. [e] Obtained from pressure increase for C_5H_8 and C_5D_8' separately; see Table II. [f] k_{HD}/k_{D_2} and $E_{D_2} - E_{HD}$ dehydrogenation mainly from C_5HD_7 in C_5D_8'. A_{HD}/A_{D_2} is obtained using the assigned activation energy, $E_{D_2} - E_{HD}$ = 1.25 ± 0.0.

from C_5H_8–C_5D_8' copyrolysis experiments. The most precise determination of k_{H_2}/k_{D_2} is obtained from H_2/D_2 formed in copyrolyses carried to 2% reaction of C_5D_8' and 5% reaction of C_5H_8, and these values are shown in Figure 3. A differentiation is made in Figure 3 between three series of mass spectrometric analyses of H_2/D_2. Product yields at greater extents of reaction were also used to calculate k_{H_2}/k_{D_2}. All of the above results are summarized in Table III in the form of Arrhenius parameters, including, in addition, a comparison with k_{H_2}/k_{D_2} calculated from pressure increase rate constants of the C_5H_8 and C_5D_8' decompositions alone (see Table II). Thus, the preferred values of the isotope effects can be represented by the equations

$$k_{HD}/k_{D_2} = (0.82 \pm 0.01) \exp(1250/RT)$$

$$k_{H_2}/k_{D_2} = (0.637 \pm 0.006) \exp(2500/RT)$$

Since there is evidence for the presence of small concentrations of radicals, among them cyclopentyl, cyclopentenyl, and cyclopentadienyl (see the following), the question might be raised concerning molecular hydrogen elimination from some of these species. Such reactions have been reported for cyclopentyl by one worker (with a rate ~13 times slower than that for ring splitting)[20a] but not by two others.[20b,c] From the ethylene and propylene analysis (~5% of ΔP) it would seem than any H_2 formed from cyclopentyl would not be important if such a reaction does occur. Molecular H_2 elimination from a cyclopentenyl radical might appear to be more favorable, since the product cyclopentadienyl has a large degree of resonance stabilization. A simple Woodward–Hoffmann analysis,[10] however, shows that such a concerted elimination does not correlate the ground state of reactant with the ground state of products for dehydrogenation of cyclopentyl or cyclopentenyl. (A correlation *is* obtained by a similar analysis for the cyclopentene system.)

In the above calculations of k_{D_2}/k_{D_2}', k_{H_2}/k_{D_2}, and k_{HD}/k_{D_2}, expressions were used in which assumptions were made of random distribution of H on $C_5H_2D_6$ and $C_5H_3D_5$ as well as of negligible secondary isotope effects. It can be shown that the error resulting from these assumptions is small, generally much less than 2%.

Ethylene and Propylene and Evidence of Radicals. Approximately 5% of the cyclopentene decomposition produced ethylene and propylene. Higher yields of these products relative to hydrogen were found for larger extents of reaction and for deuterated (relative to light) cyclopentene. A pressure effect on the total yield was observed in two copyrolysis experiments, one at 8 and the other at 20 Torr P_0 and each carried to 9 and 25% reaction in C_5D_8' and C_5H_8, respectively. In these experiments 1.6 times as much ethylene and propylene was formed at 20 than at 8 Torr. The ethylene-to-propylene ratio at 25% reaction was 1.3 in C_5H_8 and 1.7 in C_5D_8'. The addition of H_2 or D_2 (in the amount of ~4 times the ΔP) in various experiments up to 30% decomposition showed no apparent effect on total ethylene and propylene yields, or on their isotopic composition. In one experiment, D12 (Table I), C_5D_8' was decomposed to 30% completion in the

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(20) (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).

presence of an amount of added light cyclopentadiene, C_5H_6, corresponding to twice the average amount of cyclopentadiene usually formed at these experimental conditions. This addition resulted in a 1.7-fold increase in the total formation of C_2D_4' and C_3D_6'.

The isotopic composition of ethylene and propylene formed from a mixture of R–H and R–D, such as in the copyrolysis experiments or in experiment D12, was especially revealing.[17b] In all cases, there was a large amount of isotopic mixing observed in product propylene compared with very little mixing in ethylene. Thus, in the copyrolysis experiment HD2, Table I, carried to 2% decomposition in C_5D_8' and 5% in C_5H_8, $C_2H_3D/C_2H_4 = 0.04$, whereas $C_3H_5D/C_3H_6 = 0.8$.

A very small amount of isotopic mixing[17b] was also observed in the C_5 compounds, *e.g.*, in experiment HD2: $C_5H_5D/C_5H_6 < 0.001$ and $C_5H_7D/C_5H_8 = 0.001$. In experiment D12, the added C_5H_6 exhibited extensive deuterium incorporation, $C_5H_5D/C_5H_6 = 0.35$, and a sizable amount of C_5H_6 (0.11 ΔP) was reacted by undetermined paths.

Further evidence for the presence of small amounts of radicals comes from the mass spectrum at high amu of products volatile at 25° from experiment D12. At an ionization potential where little fragmentation of cyclopentene is produced, a number of low intensity peaks were found in the amu range 78–140 (scan continued to 190). The observed masses could be rationalized as originating from various isotopic combinations of methyl, allyl, cyclopentadienyl, cyclopentenyl, and cyclopentyl radicals and from fulvalene ($C_{10}H_8$). A balance of materials volatile in the reaction vessel at the end of the reaction compared with those volatile at 25° revealed a few per cent loss of material in experiment D12 but showed no such loss in experiment D11 (no added cyclopentadiene) or HD2. In addition, trace amounts of methane ($\sim$0.003 ΔP), 1,3-butadiene ($\lesssim$0.001 ΔP), cyclopentane ($\lesssim$0.001 ΔP), and a number of unidentified products of similarly low concentrations were found in gas chromatographic analyses of products formed in C_5H_8 and C_5D_8' decompositions other than experiment D12.

Discussion

The homogeneous dehydrogenation reaction occurring in the thermal decomposition of cyclopentene was found to proceed by an intramolecular, first order scission, and a quantitative determination of the small (nonmolecular) contribution of atomic hydrogen to the formation of H_2 or D_2 was made. A comparison is shown in Table IV of rate parameters for reactions of five-membered rings where dehydrogenation predominates.[3–7,21] The present results are the only ones available for the dehydrogenation reaction in cyclopentene and cyclopentene-d_8, although other workers[3] have obtained pressure increase rate contants for cyclopentene. The large increase in the value of the rate constant at 500° for the heterocyclic molecules is due mainly to their lower activation energy. Austin[6a] has shown a correlation of activation energy with product resonance energy for the series cyclopentene, 2,5-dihydrofuran, and 3-pyrroline, while a correlation with molecular parameters was shown by Wellington[7] for the above, including, in addition, 2,5-dihydrothiophene and some 1,4-cyclohexadienes. The lower activation energy for the dehydrogenation of *cis*-3a,7a-dihydroindene (postulated to proceed initially to isoindene, which rapidly isomerizes to the measured product, indene) is attributed to a much weaker C–H bond at its 3a position than the comparable C–H bond on cyclopentene.[21]

Table IV. Rate Parameters of Some Dehydrogenation Reactions

Compd	T, °C	10^4k(500°), sec^{-1}	$10^{-13}A$, sec^{-1}	E, kcal mol^{-1}	Ref
C_5H_8[a]	480–520[i]	2.89	0.63	57.8	*i*
	483–548	2.63	1.10	58.8	3a[j,k]
	416–532	2.57	2.2	59.9	3b[j,l]
	470–558	3.43	0.6	61.0	3c[j,m]
C_5D_8[b]	490–530[i]	0.892	0.99	60.3	*i*
C_6H_{11}[c]	470–512	2.54	1.79	59.6	4[n]
C_9H_{10}[d]	358–399	446	0.59	49.9	21
C_4H_6O[e]	342–409	1030	0.53	48.5	5a
C_5H_8O[f]	342–420	1510	0.68	48.3	5b
C_4H_7N[g]	320–360	5140	0.35	45.4	6a
	317–358	4690	0.19	44.6	6b
C_4H_6S[h]		54.9	1.7	54.8	7[o]

[a] Cyclopentene. [b] Cyclopentene-d_8. [c] 1-Methylcyclopentene. [d] *cis*-3a,7a-Dihydroindene. [e] 2,5-Dihydrofuran. [f] 3-Methyl-2,5-dihydrofuran. [g] 3-Pyrroline. [h] 2,5-Dihydrothiophene. [i] This work, 20 Torr. [j] Pressure increase rate constants. [k] ~110 Torr. [l] 12–30 Torr. [m] 94–200 Torr. [n] 9–11 Torr. [o] Preliminary results, no T range given.

The measurement of the isotope effect k_{HD}/k_{D_2} and k_{H_2}/k_{D_2} in this study is believed to be the first such determination in a thermally induced molecular dehydrogenation reaction. A comparison with isotope effects found in other kinetic systems[14,15,22–27] is shown in Table V. Thus at 500° the values span the range 3.2 to 1.1, from primary to secondary isotope effects. It is interesting to note that the isotope effects arising from the breaking of a single C–H bond are all in the neighborhood of 2.0. This is even the case for the H–X elimination reaction[15] which involves a transition state with some heterolytic character, as well as for the cyclopropane isomerization[23] in which the importance of the hydrogen transfer in the rate controlling step is not well established.

The complexity of the cyclopentene molecule as well as the unknown relative extents of hydrogen elimination *via* a 3,4 or 3,5 concerted step preclude a theoretical analysis of the isotope effect. The values of k_{H_2}/k_{D_2} and k_{HD}/k_{D_2} obtained in this study can, nevertheless, be taken as averages over the available paths of dehydrogenation. Valuable information concerning the behavior of the isotope effect under nonequilibrium conditions would be obtained by studying the dehydrogenation in the fall-off pressure region.[28] Most of the previous nonequilibrium kinetic studies of this

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Table V. Isotope Effect Comparison

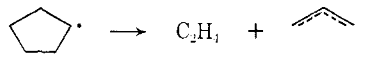
Compd(s)	k_H/k_D,[a] 500 °C	$E_D - E_H$, kcal mol^{-1}	A_H/A_D	Ref
$\frac{C_5H_8{}^b}{C_5D_8}$	3.25	2.5	0.64	*b*
$\frac{C_5HD_7{}^c}{C_5D_8}$	1.85	1.25	0.82	*c*
$\frac{CD_3 + R\text{–}H}{CD_3 + R\text{–}D}$	2.65	1.5	1.0	14
$\frac{H + H_2CO}{H + D_2CO}$	1.92	1.0	1.0	22
$CD_2HCD_2Cl^d$	2.20	1.0	1.16	15
$\frac{C_3H_6{}^e}{C_3D_6}$	1.91	1.3	0.82	23
$\frac{C_4H_6{}^f}{C_4D_6}$	1.19			24,[g] 25[h]
$\frac{C_4H_8{}^i}{C_4D_8}$	1.35	0.9	0.75	26
	1.10[j]	1.4[j]	0.44[j]	27

[a] Calculated from the Arrhenius parameters. [b] Cyclopentene H_2/D_2 formation, this work. [c] Cyclopentene-d_8 HD/D_2 formation, this work. [d] Formation of HCl/DCl per bond. [e] Cyclopropane isomerization. [f] Cyclobutene isomerization. [g] k_H measured. [h] k_D measured. [i] Cyclobutane decomposition. [j] 1.25 Torr, in first order rate constant fall-off region.

type have involved a secondary isotope effect or a primary effect for H–X elimination reactions.

The values of k_{HD}/k_{D_2} and k_{H_2}/k_{D_2} determined here may be used to correct the results obtained in the 4-cyclopentene-d_1 investigation[12] concerning the detailed mechanism of dehydrogenation, if secondary isotope effects are ignored and if it is assumed that the 3,4 and 3,5 modes of dehydrogenation have similar isotope effects. Thus, the ratio of the rate of 3,5 to 3,4 elimination of hydrogen at 550° which was reported as 12 becomes approximately 7. However, at 300°, essentially no 3,4 addition of D_2 was observed,[13] and it was suggested that the discrepancy with the previous results[12] was due to a higher activation energy for 3,4 relative to 3,5 elimination. It would be of interest to examine in addition the possibility of positional isomerization of the D atom at higher temperatures.

Because it was shown earlier that small amounts of atomic hydrogen were present, it was of interest to attempt to correlate this with the amount of ethylene formed by assuming a reaction sequence of hydrogen atom addition to the cyclopentene double bond to produce cyclopentyl[29–32] followed by reaction 2,[20] with



(2)

allyl reacting further to form propylene and other products. Thus, when both R–H and R–D are present, propylene exhibits a large degree of isotopic mixing, as is observed.

Assuming that only allylic hydrogens are involved in abstraction and that the double bonds in cyclopentadiene are as reactive toward H or D addition, per bond, as in cyclopentene, it is possible to compute pressures of ethylene formed, consistent with measured values. Table VI lists the values calculated for experiments D12 and HD-2, -5, and -1. Thus, within the approximations used and the errors involved, it is possible to show that the amounts of ethylene and propylene formed in the reaction are consistent with the amount of H and D estimated to be present.

Table VI. Estimated Yield of Ethylene

Expt[a]	$[H_2]_{At}$,[b] Torr	Ethylene yield, Torr Calcd	Max[c]	Meas
D12	0.45	0.77		1.05
HD2	0.015	0.014	0.022	0.018
HD5	0.10	0.14	0.25	0.20
HD1	0.44	0.80	1.40	0.75

[a] See text and Table I for experimental conditions. [b] Total yield of H_2 + HD + D_2 resulting from atomic hydrogen reactions. [c] Based on estimate of maximum of $[H_2]_{At}$.

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Supplementary Material Available. A listing of the following additional experimental data concerning product yields in typical C_5H_8 and/or C_5D_8' decompositions will appear following these pages in the microfilm edition of this volume of the journal: Figure 4, ratio of pressure of hydrogen formed or cyclopentene reacted to total pressure change; Table VII, relative amounts of ethylene and propylene isotopes; and Table VIII, relative amounts of cyclopentene and cyclopentadiene isotopes. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-7933.

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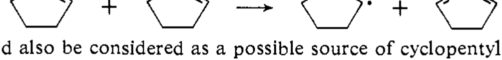
(29) The bimolecular reaction



(A)

should also be considered as a possible source of cyclopentyl. A similar initiation step has been shown to be consistent with the kinetic results for the pyrolysis of propylene[30] and 1,3-cyclohexadiene.[31] The calculated[32] enthalpy change at 500° for reaction A, 47.2 kcal mol,$^{-1}$ is much lower than the 500° value of 84.2 kcal mol^{-1} calculated for reaction B, producing hydrogen atoms.

(B)

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