of 7% longer than that in the molecule. It is reasonable to expect, therefore, that XX (or XH) is close to XX′ (or XH′). The coincidence between XX and XX′ (or XH and XH′) obtained here seems to be quite satisfactory and shows that the approximations a and b are not unreasonable.

It should be noted that the second differences in the fluorocarbon series (both molecule and radical) are not nearly as constant as the other halocarbons. Discussion of the interaction parameters for these compounds is therefore somewhat tenuous.

In the previous papers[2] it has been observed that

$$\Delta H°(2CH_3I \rightleftarrows CH_4 + CH_2I_2) = 4.7 \text{ kcal/mole} \quad (26)$$

$$DH°(CH_3\text{-}H) - DH°(CH_2I\text{-}H) = \Delta H°(CH_4 + \cdot CH_2I \rightleftarrows CH_3I + \cdot CH_3) = 0.3 \text{ kcal/mole} \quad (27)$$

and

$$DH°(CH_3\text{-}I) - DH°(CH_2I\text{-}I) = \Delta H°(CH_3I + \cdot CH_2I \rightleftarrows CH_2I_2 + \cdot CH_3) = 5 \text{ kcal/mole} \quad (28)$$

Since (26) is derived from (27) and (28), a problem is why $\Delta H°_{26}$ follows a simple bond additivity rule, while $\Delta H°_{27}$ does not. Generally

$$DH°(CH_{3-n}I_n\text{-}H) - DH°(CH_{3-n-1}I_{n+1}\text{-}H) \simeq 1 \text{ kcal/mole} \quad (29)$$

while

$$DH°(CH_{4-n}I_{n-1}\text{-}I) - DH°(CH_{4-n-1}I_n\text{-}I) \simeq 6 \text{ kcal/mole} \quad (30)$$

This can be explained as follows. Both (29) and (30) are expressed in terms of CX, XX, etc., through the relations in (10)–(13) and (18)–(21). They are finally approximated by (29) ≈ IH and (30) ≈ II − IH, since II ≈ II′ and IH ≈ IH′. Both IH ≈ 2, and II − IH ≈ 7 kcal/mole agree with (29) = 1 and (30) = 6 kcal/mole, respectively.

The data for II, II′, IH, and IH′ come from the same sources as eq 26–30, so this agreement is not surprising. However, formulation of (29) and (30), in terms of the interaction parameters of the Bernstein scheme, makes the differences in BDE's physically understandable.

For difference in bond strengths, such as (30), the number of I–I interactions change so that the difference is far from zero. For differences like (29), where only the transfer of a hydrogen atom occurs, it is the number of I–H interactions (a quantity much smaller than I–I) which changes and the difference is small.

The Thermal Decomposition of 6-Methyl-3,4-dihydro-2H-pyran[1]

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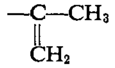
Received October 7, 1968

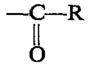
Abstract: The gas-phase thermal decomposition of 6-methyl-3,4-dihydro-2H-pyran (6-MDHP) into ethylene and methyl vinyl ketone has been investigated over the temperature range 330–370° and at initial pressures of 5–25 mm. The reaction is a first-order homogeneous process and is not affected by the addition of nitric oxide or propylene. An activation energy of 51.2 ± 0.5 kcal/mole has been found and the first-order rate constant is $k = 2.82 \pm 0.09 \times 10^{14} \exp(-51{,}200/RT)$ sec^{-1}. 6-MDHP has been found by gas chromatography to be among the products formed in the decomposition of methyl cyclobutyl ketone.

The thermal decomposition of several derivatives of cyclopropane and cyclobutane (*i.e.*, those derivatives with



$$-\underset{\underset{CH_2}{\|}}{C}-CH_3$$

and



$$-\underset{\underset{O}{\|}}{C}-R$$

where R is H and CH_3) have been found to yield corresponding five- and six-membered ring compounds. Isopropenylcyclobutane[3] gave nearly equal amounts of ethylene–isoprene and 1-methylcyclohexene. Roquitte[4] established that a small amount of 3,4-dihydro-2H-pyran was formed during the decomposition of cyclobutanecarboxaldehyde. In contrast, no ring-enlargement reaction was reported for the decomposition of methyl cyclobutyl ketone.[5] Our present reinvestigation of the decomposition products of this compound by means of gas chromatography indicates the presence of a very small amount of a ring-enlargement product, 6-methyl-3,4-dihydro-2H-pyran (6-MDHP). Subsequently, the decomposition of 6-MDHP has been studied in some detail.

Experimental Section

Materials. Two methods were used to prepare 6-methyl-3,4-dihydro-2H-pyran (6-MDHP). Sample I was obtained by de-

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

[2] Abstracted by C. S. Caton from her M.S. thesis written under the supervision of the late W. D. Walters, University of Rochester, 1967. Address correspondence to author at 255 Dolly Varden Blvd., #38, Scarborough 722, Ontario, Canada.

[3] R. J. Ellis and H. M. Frey, *Trans. Faraday Soc.*, **59**, 2076 (1963).

[4] B. C. Roquitte and W. D. Walters, *J. Am. Chem. Soc.*, **84**, 4049 (1962).

[5] L. G. Daignault and W. D. Walters, *ibid.*, **80**, 541 (1958).

hydration of 6-hydroxy-2-hexanone[6] in benzene. Following the removal of the azeotrope, the material was fractionally distilled on a spinning-band column. A middle fraction (bp 108.8° at 749 mm) was analyzed on a Perkin-Elmer "A" column (diisodecyl phthalate on a Celite base) and found to contain 96.5% 6-MDHP and 3.5% benzene. The synthesis of sample II was accomplished according to the directions of Perkin[7] with modifications suggested by Montaigne[8] and Gol'mov.[9] 1-Chloro-3-bromopropane was refluxed with sodium acetate for about 4 hr. The 6-methyl derivative of the cyclic ester was saponified in a solution of potassium hydroxide in ethyl alcohol. The melting point of the recrystallized acid derivative was found to be 118° (lit.[7] 119°). *Anal.* Calcd for acid derivative: C, 59.14; H, 7.09. Found: C, 58.66; H, 7.07.[10] Decarboxylation of the acid derivative[7] yielded 6-MDHP which was found by gas chromatography to be 99.5% pure. The refractive index of 6-MDHP given in the literature[8] as $n^{15}\text{D}$ 1.4485 may be compared with $n^{15}\text{D}$ 1.4480 for sample II. A further purification was carried out on a small portion of sample II by refluxing it under vacuum over a doubly distilled sodium mirror on a Pyrex tube. The material treated in this manner will be referred to as sample IIa. The infrared spectra obtained on a Perkin-Elmer 421 instrument of samples I and II were virtually identical. The nuclear magnetic resonance spectra of samples I and II measured on a Varian A-60 instrument were identical except for a small peak attributable to benzene in the spectrum of sample I.

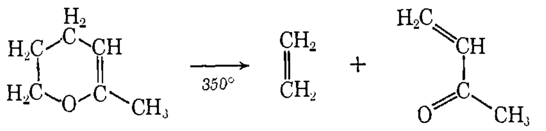
Methyl cyclobutyl ketone prepared by Daignault[5] and stored under vacuum was found by gas chromatography to be 99.5% pure. Both this sample of methyl cyclobutyl ketone and sample II of 6-MDHP were tested for the presence of peroxides with a sensitive ferrous ion–thiocyanate reagent. In neither case was further treatment deemed necessary. 3,4-Dihydro-2H-pyran supplied by Eastman Kodak was distilled on a spinning-band column. Final purification by gas chromatography yielded material with a purity of greater than 99.5%. Methyl vinyl ketone supplied by Aldrich with a purity of 96%, ethylene (99.9%, Phillips), and propylene (99.9%, Ohio) were used. Nitric oxide (99%, Matheson) was distilled under vacuum two times between traps at −159 and −196° prior to its use in this study.

Apparatus and Technique. The apparatus employed in this study has been previously described.[11] During the course of the present study the platinum—platinum-13% rhodium thermocouple used to measure the temperature in the reaction vessel was standardized against the melting point of zinc (419.5°) supplied by the National Bureau of Standards. Both a packed reaction vessel B (276 ml) and an unpacked vessel A (355 ml) were used. Vessel B was packed with Pyrex tubes to increase the surface-to-volume ratio by about sevenfold. Changes in pressure were measured to within ±0.01 mm with a Gaertner cathetometer. External tubing connected to the reaction vessel was heated electrically, and tests showed that no detectable amount of material was absorbed by the stopcock grease. The surface of the reaction vessel was "poisoned" periodically with either isobutylene or 3-methyl-1-butene. Generally a preliminary pyrolysis was performed in order to ensure a deactivated surface of the reaction vessel. No reaction between methyl vinyl ketone and ethylene was indicated by pressure change when an amount of each substance was introduced into the reaction vessel at a temperature in the range used for decomposition of 6-MDHP. This mixture was subsequently analyzed by gas chromatography, and no methyldihydropyran was detected.

Analyses. The reaction mixture was removed usually after about 30% decomposition and separated into three fractions: (a) material volatile at −196°, (b) substances volatile at −78° and condensible at −196°, and (c) substances condensible at −78°. Fraction a accounted for not more than 0.1–0.2% of the pressure increase (ΔP) and was not analyzed. Fraction b was identified as ethylene by infrared analysis on a Perkin-Elmer 421 instrument in a 1-l. gas cell with a 1-m path length. Furthermore, a Perkin-Elmer 154D vapor fractometer equipped with a Golay R column and flame ionization detector indicated that the most volatile component of the condensible reaction mixture had the same retention time as that of ethylene (4 min).

Chromatographic studies using a 150-ft Golay R column, a 2-m "A" column, and a 2-m "R" column (containing 13% by weight UCON LB 550-X oil on a GC-22 base supplied by Coast Engineering Laboratory), the latter two with the thermal detector, showed that the reaction mixture, in addition to peaks identified as undecomposed 6-MDHP and ethylene, contained only one other chromatographic peak, which had the same retention time as methyl vinyl ketone. The infrared spectrum of fraction c was consistent with the evidence that both 6-MDHP and methyl vinyl ketone were present. A polarographic determination made on a Sargent Model XV polarograph of fraction c gave a half-wave potential (*vs.* pool) within 0.02 V of that found for a solution of Aldrich methyl vinyl ketone. Methyl vinyl ketone exhibits a broad ultraviolet absorption from 210 to 218 mμ with a maximum at 212.5–213 mμ in aqueous solution containing 0.5% methanol. Using a Beckmann DU spectrophotometer to analyze fraction c, a strong absorption appeared, but no maximum was reached. 6-MDHP was found to absorb in increasing amounts throughout that range.

The product analyses indicate that the homogeneous thermal decomposition of 6-MDHP occurs as



(1)

The occurrence of reaction 1 in a constant-volume system necessitates that the pressure increase ΔP (observed pressure change corrected for "dead space") equal the pressure of ethylene formed. The pressure of ethylene (P_E) at reaction temperature was calculated from the amount of fraction b determined by gas buret. Table I summarizes some of the data, which give an average value of $P_E/\Delta P$ = 0.99 ± 0.02. This value is essentially that predicted by reaction 1; therefore, the use of pressure measurements to record the extent of reaction seems justified.

Table I. Pressure Increase Compared with the Pressure of Ethylene Formed during the Pyrolysis of 6-Methyl-3,4-dihydro-2H-pyran

Temp, °C	P_0, mm[a]	ΔP, mm[b]	P_E, mm
359	21.04	7.37	7.40
359	6.28	2.12	2.14
338	18.51	5.76	5.61
339	10.84	2.63	2.57

[a] Initial pressure of 6-methyl-3,4-dihydro-2H-pyran. [b] All pressures in this study are in terms of mercury at 26°.

Results

Order and Homogeneity of the Reaction. The general appearance of the pressure–time curves indicated that the decomposition might be a first-order reaction in that there was neither a significant induction period nor an inflection point. Furthermore, the slope of the plot $\log [P_0/(2P_0 - P_t)]$ *vs.* time was found to yield a straight line, and the rate of the reaction was not affected by a fourfold change in initial pressure.

The time corresponding to 25% decomposition, $t_{1/4}$, was obtained from the pressure–time curves after correcting for "dead space." For the 37 experiments used to calculate k, a value of $t_{1/4}/t_{1/8}$ was found to average 2.12 ± 0.03 which is reasonable agreement with the theoretical value of 2.15 for a first-order reaction. As can be seen in Figure 1, no significant change in the rate data occurred when S/V was increased seven times by substituting the packed vessel. The rate constants in experiments with added propylene and nitric oxide are in agreement with those for pure 6-MDHP under similar conditions. Thus, the reaction appears to be a

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(7) W. H. Perkin, *J. Chem. Soc.*, **51**, 702 (1887).

(8) J. C. Montaigne, *Ann. Chim.* (Paris), **9**, 310 (1954).

(9) V. P. Gol'mov and V. N. Balakhontsura, *Chem. Abstr.*, **54**, 19476, (1960).

(10) Performed by Micro-Tech Laboratories, Inc., Skokie, Ill.

(11) M. Zupan and W. D. Walters, *J. Phys. Chem.*, **67**, 1845 (1963); M. Zupan and W. D. Walters, *J. Am. Chem. Soc.*, **86**, 173 (1964).

Table II. First-Order Rate Constants for the Decomposition of 6-Methyl-3,4-dihydro-2H-pyran under Various Conditions[a]

Temp, °C	P_0, mm[b]	10^4k, sec^{-1}	Added gas,[c] mm
358.8	13.34	5.90	4.46 P
358.8	21.95	5.83	5.35 P
358.7	21.04	5.85	
359.0	26.81	6.09	5.13 P
359.9	13.65	6.05	0.25 NO
359.9	23.29	6.12	
339.4	20.32	1.61	8.32 P
339.4	13.22	1.68	4.41 P
339.9	16.86	1.58	0.25 NO
339.5	19.45	1.60	
339.7	8.64	1.63	
339.7	10.23	1.65	

[a] All experiments were performed in the unpacked vessel on sample II. [b] Initial pressure of 6-methyl-3,4-dihydro-2H-pyran plus added gas. [c] P and NO refer to propylene and nitric oxide, respectively.

first-order homogeneous reaction with no evidence for free-radical chain processes (see Table II).

Kinetic Test of Purity. Two experiments were performed on sample IIa (material refluxed over a doubly distilled sodium suface). Rate constants calculated for these experiments were in agreement with those for samples II and I (after a correction was made for the presence of 3.5% benzene).

Activation Energy. The temperature dependence of the rate of decomposition of 6-methyl-3,4-dihydro-2H-pyran (6-MDHP) over the temperature range 330–370° is shown in the Arrhenius plot of log k *vs.* $1/T$ (Figure 1). Thirty-seven experiments with initial pressures from 5 to 25 mm were used to obtain a value of the activation energy. The slope of the best straight line drawn by inspection through the experimental points indicated an activation energy of 51.2 kcal/mole, and a least-squares analysis of the data with an IBM 650 computer gave an activation energy of 51.2 ± 0.5 kcal/mole. With $E = 51.2$ kcal/mole the average value of A is equal to $2.82 \pm 0.09 \times 10^{14}$ sec^{-1}. Equating this value of A to $\kappa e(kT/h) \exp(\Delta S^{\ddagger}/R)$ and assuming κ to be unity, a value of 3.9 eu at 360° is obtained for $\Delta S^{\ddagger}$.

Methyl Cyclobutyl Ketone Analysis. A further analysis by gas chromatography of the reaction products resulting from the methyl cyclobutyl ketone decomposition was undertaken in order to determine whether any ring-enlargement products were formed. In the course of this analysis the rate constants and stoichiometric measurements reported by Daignault[10] were verified. The gas chromatographic analyses were made using a Perkin-Elmer "A" column and the previously described "R" column with the thermal detector. In addition, a more sensitive analysis was obtained using a Perkin-Elmer 2-m "R-X" column (polypropylene glycol on Chromosorb) with the flame ionization detector. Confirmation of the presence of a small amount of 6-methyl-3,4-dihydro-2H-pyran (6-MDHP) appeared with all three systems. Owing to the small amount of material, identification by a technique other than gas chromatography has not been undertaken. From a comparison of the peak areas, the ratio of the amount of 6-MDHP to the amount of methyl cyclobutyl ketone that exists after approximately one-fourth decomposition is 10^{-3}. At temperatures of 370 and 380° the rate of decomposition of methyl dihydropyran is nine to ten times faster than the decomposition of methyl cyclobutyl ketone. If the decomposition of methyl cyclobutyl ketone into methyl vinyl ketone and ethylene proceeded entirely through the formation of 6-MDHP, a ratio of methyl cyclobutyl ketone to 6-MDHP of 0.1 would be required to account for the total amount of methyl vinyl ketone formed. Thus, not more than 1% of the methyl vinyl ketone formed was *via* the decomposition of 6-MDHP.

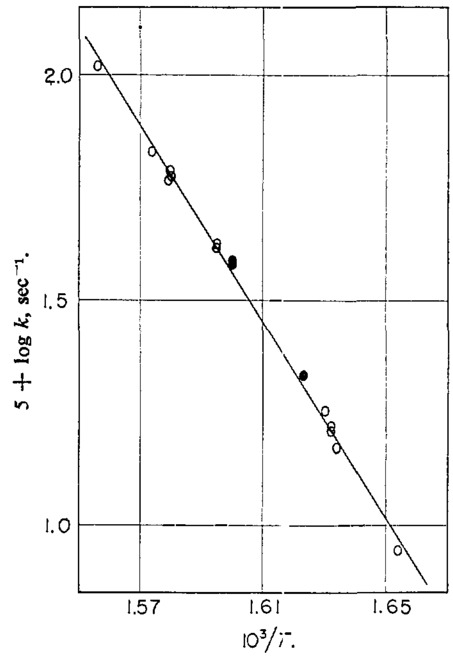
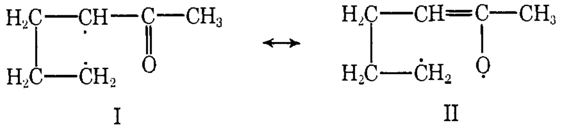


Figure 1. First-order rate constants for the decomposition of 6-methyl-3,4-dihydro-2H-pyran at various temperatures; initial pressure 8–16 mm: ○, unpacked vessel; ●, packed vessel.

Discussion

The results of this study show that the decomposition of methyl cyclobutyl ketone is similar to that of cyclobutanecarboxaldehyde, with the ring-enlargement process constituting a minor part of the reaction. The relative amount of ring-enlargement product formed from cyclobutanes containing $-C(=O)R$ (where R is H or CH_3) differs significantly from the amount formed from cyclobutane containing $>C=C(CH_3)-$. In order to explain the nearly equal amounts of ethylene–isoprene and 1-methylcyclohexene resulting from the decomposition of isopropenylcyclobutane, Ellis and Frey propose a biradical mechanism. The formation of a similar biradical may explain the decomposition of methyl cyclobutyl ketone.



(2)

The resonant structures I and II are not equivalent in that I contains a carbon–oxygen double bond while II has a carbon–carbon double bond. The resonance stabilization energy, therefore, would reasonably be less than the 12–15 kcal/mole Ellis and Frey assigned to the biradical resonance in the isopropenylcyclobutane decomposition. The fact that the activation energy of methyl cyclobutyl ketone decomposition is about 3 kcal/mole greater than the activation energy of the isopropenylcyclobutane decomposition is consistent with this reasoning.

There is no *a priori* reason why the same mechanism, *i.e.*, formation of a biradical, used to explain the decomposition of methyl cyclobutyl ketone and concurrent formation of 6-methyl-3,4-dihydro-2H-pyran (6-MDHP) must also explain the decomposition of 6-MDHP which occurs under very similar conditions of temperature and pressure. If the decomposition of 6-MDHP results in the formation of the above biradical structures, the formation of methyl cyclobutyl ketone should be possible. The study of the decomposition of 6-MDHP, however, detected no methyl cyclobutyl ketone formation.

The rate constants for 6-MDHP and 3,4-dihydro-2H-pyran[12] over the temperature range 330–370° show that the 6-MDHP decomposition proceeds approximately 45% faster. In order to determine the change in activation energy caused by methyl substitution, a value of $10^{14.542}$ for A was assigned to both reactions and corresponding values of E were calculated. At 360° the activation energy of the methyl derivative was 0.7 kcal/mole less than that of dihydropyran. Murphy, *et al.*,[13] studied the isomerization of vinyl allyl ether and isopropenyl allyl ether and found the methyl derivative to have a 1.3 kcal/mole lower energy.

A comparison of the decomposition of the substituted and unsubstituted dihydropyrans with the decomposition of cyclohexene[14] indicates the former reactions to be less complicated by free radicals. This is undoubtedly due to the fact that dihydropyrans decompose at about 350°, while temperatures near 500°, which greatly increase the probability of free radical formation, are necessary for the decomposition of cyclohexene.

Acknowledgment. The author wishes to express her indebtedness to the late Professor W. D. Walters who suggested this study and supervised its progress. She wishes to thank Mr. Carl Whiteman for the use of his least-squares program and General Railway Signal Co. for the use of their IBM computer.

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Competitive Reactions of the Excited Oxygen Atoms, O(^{1}D)

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Received May 1, 1969

Abstract: Competitive interaction of O(^{1}D) atoms, formed by photolysis of N_2O at 2139 Å, with neopentane and a number of other gases has been studied at room temperature. Formation of the ground-state oxygen atoms, O(^{3}P), in these experiments was followed by measuring the characteristic products of their addition to butene-1. It was found that under the conditions employed SF_6 and He did not interact with O(^{1}D), H_2, CH_4, and neopentane reacted to form products but did not deactivate O(^{1}D), while N_2, Xe, CO, and CO_2 deactivated O(^{1}D) to O(^{3}P). The rates of these processes, relative to the rate of reaction of O(^{1}D) with neopentane, k_5/k_2, were determined from the decrease in the yields of neopentanol when another gas was added. The k_5/k_2 values obtained (given in parentheses) are: neopentane (1.000), SF_6 (0), He (0), H_2 (0.254), CH_4 (0.315), N_2 (0.039), Xe (0.128), CO (0.074), CO_2 (0.126). Where a comparison is possible, the trend is in good agreement with the previous results from this laboratory obtained in very different systems. Carbon monoxide does not show an exalted reactivity toward O(^{1}D) atoms and, moreover, does not, under the conditions employed, chemically react with them to form CO_2 but deactivates them to the ground state, O(^{3}P).

The chemical behavior of the electronically excited oxygen atoms, O(^{1}D), is of considerable interest, and several studies of the interaction of O(^{1}D) with various gases have been reported in recent years. There is, however still a great deal of controversial information about the relative rates of these interactions and uncertainty whether they result in a collisional deactivation of O(^{1}D) to O(^{3}P), a reaction to form products, or both. It is necessary, therefore, to obtain further experimental information on these processes using as many different experimental techniques and sources of O(^{1}D) as feasible.

In earlier work in this laboratory with propane[1] and isobutane,[2] it has been established that in general O(^{1}D) reacts with paraffins in the following two ways: (a) by insertion into the CH bonds to form vibrationally "hot" alcohols which decompose or are stabilized depending on the pressure and the number of vibrational degrees of freedom of the paraffin and (b) by abstraction of hydrogen from the paraffin to form OH and alkyl radicals. The number of final products arising from all possible interactions and the direct photolysis of the initial products depends on the type of paraffin (with primary, secondary, or tertiary hydrogens) and could be quite large.[2] In a more recent study of the interaction of O(^{1}D) with neopentane,[3] it has been found, as might have been expected in view of the sym-

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