pure hydrolysis products will be obtained by crystallization procedures in view of the complexity of the system.

It is to be noted that these acid hydrolysis reactions provide a means for the isotopic exchange of chloride ligands with chloride ion in the solution. The use of radioactive chlorine-36 therefore may possibly give information which will clarify some of the stereochemical features of the reaction. There is also the question whether isotopic exchange may take place by alternative mechanisms. The authors are conducting exchange experiments with Cl^{36} which will be reported at a later date.

Acknowledgment.—We wish to thank Dr. F. Basolo for providing us prior to publication with information concerning the kinetics of other complexes of platinum.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Thermal Decomposition of Methyl Cyclobutyl Ketone[1,2]

BY LOUIS G. DAIGNAULT AND W. D. WALTERS

RECEIVED SEPTEMBER 3, 1957

The vapor-phase thermal decomposition of methyl cyclobutyl ketone has been investigated over the temperature range 360–410°. During the initial stages of the reaction ethylene and methyl vinyl ketone, which are the only important products, were found to be present in essentially equivalent amounts. On the basis of experiments at pressures from 10 to 65 mm. and from data taken during the course of the decomposition the reaction is first order. No appreciable inhibition of the decomposition by propylene, toluene or nitric oxide was observed. Experiments with initial pressures near 50 mm. gave an activation energy of 54.5 kcal./mole. The first-order rate expression is $k = 3.4 \times 10^{14} e^{-54500/RT}$ sec.$^{-1}$.

The thermal decompositions of methyl alkyl ketones have been observed to proceed by free radical chain processes.[3] On the other hand cyclobutane[4] and several other four-membered ring compounds[5,6] appear to undergo simple ring cleavage reactions which are not inhibited by propylene, toluene or nitric oxide. Therefore, the investigation of the thermal decomposition of methyl cyclobutyl ketone was of interest, particularly for comparison with the behaviors of these related compounds. Moreover, the photochemical decomposition of methyl cyclobutyl ketone has been investigated at 2654 Å. with temperatures from 60 to 250°.[7] Carbon monoxide, ethylene, methane and cyclobutane are the principal products, but at the lower temperatures methylcyclobutane, ethane and cyclobutene are present also. Free radical processes were used to explain the formation of the products.

Experimental

Materials and Apparatus.—The methyl cyclobutyl ketone was prepared by passing a mixture of cyclobutanecarboxylic acid and acetic acid (1:2.5 mole ratio) over a manganous oxide catalyst at 380–390° and collecting the products in a receiver cooled to −78°.[8] A number of samples were prepared and purified. In the first two preparations the sample was separated into fractions by distillation in a Claisen flask. Rate measurements were made with the fourth fraction of the first preparation (A-4) and a small fraction (B) taken after the distillation of 60% of the second sample. In the third preparation the fourth fraction from the first distillation was fractionated in a small column equipped with Podbielniak Heligrid packing. Sample C-4c was the third fraction. The D samples were from the fourth preparation after distillation in a Claisen flask and fractionation in a nitrogen atmosphere at a reflux ratio greater than six to one in a column with 85 cm. of Lecky-Ewell packing. Sample D-2 was one which was purified by conversion to the semicarbazone, recrystallization, and regeneration of the ketone. The melting point of the semicarbazone was 148.0–148.5°; literature value, 148–149°.[9] Sample D-5 was a portion of the fifth fraction placed directly on the vacuum line and used for rate studies. Sample D-5a was a portion placed in storage at about −15°; after seven months' storage plus some contact with air this sample gave a peroxide test with the sensitive ferrous ion–thiocyanate reagent. Before this sample was used in a few experiments the peroxides were reduced to a hardly detectable level by long shaking with mercury. The infrared absorption spectra of samples B, D-2 and D-5 were obtained in a one-meter gas cell with Perkin–Elmer models 12AB and 21 infrared spectrometers. Since the spectra from the three samples were in agreement, no indication of the presence of an impurity was obtained. None of the fractions used for kinetic measurements had a boiling range in excess of 0.2° and in most cases the boiling point was constant (within 0.1°) during the collection of the sample. The indices of refraction ($n^{20}\text{D}$) for the various samples were: B, 1.4322; C-4c, 1.4317; D-2, 1.4321; D-5, 1.4322. The index of refraction has been reported as 1.4322 at 19.3[9a] and 1.4315 at 20°.[10]

Propylene (99.5%) was obtained from the Ohio Chemical and Surgical Equipment Co. Toluene (Mallinckrodt analytical reagent) was dried over anhydrous calcium sulfate. In general all compounds were degassed immediately prior to use. Nitric oxide (Matheson) was distilled under vacuum two times. Before each use the nitric oxide was degassed at −196° and then distilled from a storage bulb (placed in a bath at −78°) into a small tube at −196°.

The furnace, temperature control, and vacuum system were similar in design to those described earlier.[11] For the study of surface effects the cylindrical Pyrex reaction vessel (310 ml.) was replaced by one packed with thin-walled Pyrex tubing which increased the surface-to-volume ratio 28-fold. The temperature at the center of the reaction bulb was

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[1] This work was supported by the Celanese Corporation of America during the summer of 1954 and by the National Science Foundation from 1955 to 1957.

[2] Abstracted from the Ph.D. thesis submitted by Louis G. Daignault.

[3] (a) F. O. Rice and O. L. Polly, *J. Chem. Phys.*, **6**, 273 (1938); (b) J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A183**, 33 (1944); (c) C. E. Waring and M. Spector, THIS JOURNAL, **77**, 6453 (1955); (d) C. E. Waring and V. L. Garik, *ibid.*, **78**, 5198 (1956); (e) W. T. Barry, Jr., and W. D. Walters, *ibid.*, **79**, 2102 (1957).

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[5] R. E. Wellman and W. D. Walters, *ibid.*, **79**, 1542 (1957).

[6] M. N. Das, F. Kern, T. D. Coyle and W. D. Walters, *ibid.*, **76**, 6271 (1954).

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[8] N. Zelinskiĭ and E. Riachina, *Ber.*, **57B**, 1932 (1924); B. A. Kazanskiĭ, *ibid.*, **69B**, 952 (1936).

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measured by means of a platinum, platinum–13% rhodium thermocouple connected to a Leeds and Northrup type K-2 potentiometer. The thermocouple was standardized on three occasions at the melting point of zinc (419.5°) obtained from the National Bureau of Standards. Pressures were measured in some experiments with a heated mercury manometer (~3 mm. i.d.) and in other experiments (especially those at 10 mm.) with a heated 19 mm. bore mercury manometer which was read with a Gaertner cathetometer (M930-300 or a modified M303). Stopcocks adjacent to the reaction vessel were heated electrically to prevent the condensation of liquids and lubricated with Convacene-S high-vacuum grease.

Products of the Reaction—The reaction mixture was separated into four fractions: (1) gases volatile at −196°; (2) gases volatile at −139°, but condensable at −196°; (3) substances volatile at −78°, but condensable at −139°; (4) substances non-volatile at −78°. Since essentially all of the products were found in fractions (2) and (4), the identification of these fractions will be considered first. By the use of a Perkin–Elmer infrared spectrometer 12AB with a one-meter gas cell an infrared absorption curve was obtained for fraction (2) from a 20 mm. experiment at 429° with a reaction time of 10 min. The absorption peaks were similar to those reported in the literature for ethylene[12] and also corresponded to those of pure ethylene determined on the same instrument. Moreover, fraction (2) from an experiment in the packed bulb had an infrared absorption spectrum in agreement with that of ethylene. On the basis of volatility the products in fraction (2) would be expected to be mainly C_2 compounds. That fraction (2) was almost all olefin was indicated by the fact that in two 25 mm. experiments carried to 50–60% decomposition at 400° at least 97% of fraction (2) could be absorbed in activated sulfuric acid.[13] A mass spectrometric analysis[14a] was obtained for fraction (2) from a 64 mm. experiment in the unpacked bulb after 35% decomposition at 380°. A mass spectrometric analysis[14b] was made also on fraction (2) from a packed bulb experiment, 46 mm., 57% decomposition at 400°. The results of the mass spectrometric analyses (in %) may be summarized as follows with the parentheses denoting the packed bulb experiment: ethylene, 99.4 (99.3); ethane, 0.1 (0.0); acetylene, 0.0 (0.2); propylene 0.1 (0.2); propane and higher paraffins, 0.03 (0.2); butenes, 0.2 (0.2); other C_4 compounds, 0.2 (trace). In agreement with the other analyses the data show that fraction (2) is almost entirely ethylene.

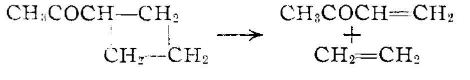
Fraction (4) would be expected to contain liquid products and undecomposed methyl cyclobutyl ketone. From a 31 mm. experiment carried to ~50% pressure increase at 401° the more volatile portion of fraction (4) was subjected to infrared absorption analysis in a one-meter gas cell. Absorption peaks were found at 5.9, 7.0–7.3, 8.0, 8.5 and 10.5 μ. The absorptions corresponded to those found for pure methyl vinyl ketone with the same instrument and also those given in the literature.[12] The important product in fraction (4) (not considering undecomposed methyl cyclobutyl ketone) was identified by two other methods. With a Beckman DU spectrophotometer a large absorption maximum was found in the region 207–215 mμ in accord with that observed for a pure sample of methyl vinyl ketone and also reported in the literature.[15] After a solution of the reaction products in a supporting electrolyte (90% water, 10% methanol, and 0.1 *N* KCl) was prepared, a polarographic analysis[16] was performed with a Fisher Elecdropode The half-wave potential was found to agree within the limits of experimental error (0.02 v.) with the half-wave potential for pure methyl vinyl ketone measured under similar conditions. Therefore, the main products in the early stages of the decomposition are ethylene and methyl vinyl ketone in equivalent amounts, as data to be presented later will show.

In many experiments volume measurements were made on fraction (1) The majority of the preliminary experiments at 10 mm. initial pressure indicated that the amount of gas non-condensable at −196° does not represent more than 0.7% of the total products at 25% decomposition. Thirteen 40–60 mm. experiments were performed later in the unpacked bulb over the temperature range 360–410° at decompositions of 25–30%. Fraction (1) was observed to average not more than 0.2% of the total products. (It was assumed that as much methyl vinyl ketone was formed as ethylene.) In seven experiments in the packed vessel under similar conditions fraction (1) was 0.3–0.4% of the total products. In the case of fraction (3) the results of three experiments (50–60% decomposition) indicated that the volume of fraction (3) amounted to less than 0.2% of the total volume of products for each experiment.

Two experiments were performed in an attempt to determine whether or not significant quantities of ketenes are produced in the pyrolysis of methyl cyclobutyl ketone. In each case a solution of the products in freshly boiled water was titrated with standard base solution to the phenol red endpoint. Both experiments at about 50 mm. pressure were carried to approximately 25% decomposition at 400°. Since only one drop of base was required for the titration and one drop for a comparable blank, no positive evidence was obtained for ketene in either case. If one considers the maximum possible titration error and the normality of the base (more dilute in the second experiment), it is estimated that ketene corresponding to 0.5% of the total products in the first experiment and 0.1% in the second experiment might have been present without detection.

For the determination of the amounts of the products formed, the reaction mixture was removed after a definite time and separated into fractions as described above. Since there were essentially no products in fraction (3), a combined fraction (2) and (3) was measured in a gas buret and designated as ethylene. The quantitative analysis of methyl vinyl ketone in fraction (4) was accomplished in two ways. A solution of fraction (4) was prepared and divided into two parts. For one part of the solution the wave height of the polarogram was compared to that of a freshly prepared standard solution of methyl vinyl ketone which was analyzed immediately after the unknown solution. The second portion of the solution was diluted with water and the optical density at 213 mμ measured by the use of the Beckman DU spectrophotometer. After the application of a small correction for the absorption of the undecomposed methyl cyclobutyl ketone the concentration of methyl vinyl ketone was calculated by the use of the molar extinction coefficient obtained under similar conditions for standard solutions. In most of the experiments both polarographic and spectrophotometric determinations of methyl vinyl ketone were made and good agreement was obtained.

Stoichiometry.—The qualitative analyses indicated that the decomposition follows the equation



$$\begin{array}{l}CH_3COCH—CH_2\\ \quad\quad\quad\ |\quad\quad\ \ |\\ \quad\quad\quad CH_2—CH_2\end{array} \longrightarrow \begin{array}{c}CH_3COCH{=}CH_2\\ +\\ CH_2{=}CH_2\end{array} \qquad (1)$$

In order to ascertain whether the reaction proceeds stoichiometrically according to equation 1, experiments were performed under various conditions and the reaction mixtures were analyzed. Typical results are shown in Table I where the pressure in mm. of product refers to the amount that was present in the reaction vessel at the time the mixture was removed. The values in the last column are usually the averages of the polarographic and spectrophotometric determinations. ΔP is the increase in the total pressure. The experimental data from twenty-two experiments show that the average values of (mm. $C_2H_4/\Delta P$) and (mm. $CH_3COC_2H_3/\Delta P$) are 0.98 ± 0.08 and 1.02 ± 0.05, respectively. It is to be noted that the smaller value for ethylene could possibly be due to the loss of ethylene by solution in the methyl vinyl ketone and methyl cyclobutyl ketone in the −78° trap. Since the ratios correspond to unity within the experimental error of the analyses, the primary decomposition appears to proceed quantitatively as shown in equation 1. Moreover, the data indicate that the measurements of the pressure increase may be used to follow the

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(12) Infrared Spectral Data, American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, Curves 18 and 530 for ethylene and Curve 760 for methyl vinyl ketone.

(13) W. J. Gooderham, *J. Soc. Chem. Ind. (London)*, **57**, 388T (1938).

(14) (a) Performed by the Consolidated Engineering Corporation; (b) analysis by R. C. Wilkerson of the Celanese Corporation of America.

(15) Ultraviolet Spectral Data (Curves 345 and 346), American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

(16) E. I. Fulmer, J. J. Kolfenbach and L. A. Underkofler, *Ind. Eng. Chem., Anal. Ed.*, **16**, 469 (1944)

TABLE I

ANALYSES OF THE PRODUCTS OF THE DECOMPOSITION OF METHYL CYCLOBUTYL KETONE

P_0, mm.	ΔP, mm.	C_2H_4,[a] mm.	$CH_3COC_2H_3$, mm.
Temp., 410°			
9.1	2.5	2.9	2.8
48.3	15.0	13.3	15.1
Temp., 400°			
10.8	2.9	3.1	3.1
41.6	11.6	10.6	11.7
56.6	18.1	18.0	18.3
57.4	31.6	32.1	31.5
59.4	32.6	33.8	33.3
64.9	20.5	18.7	19.6
47.0[b]	14.8[b]	13.8	15.1
50.6[c]	15.9[c]	14.9	15.5
57.6[d]	18.8[d]	18.3	18.9
Temp., 390°			
10.8	2.7	2.9	2.9
49.2	14.1	12.4	14.1
Temp., 380°			
13.2	3.3	..	3.6
44.2	13.0	12.2	12.6
51.8	13.9	13.0	13.7
Temp., 370°			
11.7	3.2	3.4	3.4
54.0	14.5	12.4	14.4
Temp., 360°			
55.1	13.7	13.3	13.4

[a] Includes all gases in fractions (2) and (3). [b] 1.3 mm. nitric oxide added. [c] 0.7 mm. nitric oxide added. [d] Packed vessel.

rate during the initial stages of the decomposition. Likewise the presence of nitric oxide or added surface (28 × S/V) does not alter the stoichiometry of the primary reaction. The various samples of methyl cyclobutyl ketone gave results which were the same within the expected error of the analytical methods. Experiments were also performed at 400° with 33–49 mm. methyl cyclobutyl ketone and 18–28 mm. propylene or toluene. After one-third of the methyl cyclobutyl ketone had decomposed, the ratios (mm. $C_2H_4/\Delta P$) and (mm. $CH_3COC_2H_3/\Delta P$) in two experiments in the presence of toluene averaged 0.94 and 1.03, respectively. In the presence of propylene each ratio was found to average 0.97. Within the experimental error of the analyses the ratios seem to have the value of 1 in the presence of toluene or propylene indicating that the decomposition still follows equation 1.

In a test of the stability of the product methyl vinyl ketone, 8 mm. of this compound was observed to give only 2–3% pressure increase after 20 min. at 400°. The half-time for the methyl cyclobutyl ketone decomposition is about 17 min. at 400°. It had been found earlier in this Laboratory that at 400° ethylene alone should not react to any significant extent. Therefore, under the experimental conditions the pressure measurements should not be influenced appreciably by the decomposition of the major products for at least the first half of the reaction. That the primary products react slowly in the later stages of the decomposition is evidenced by the fact that the gases noncondensable at −196° amounted to about 9% of the products formed after 11 half-times at 400° in a 40 mm. experiment. That two molecules are produced from each molecule of reactant was indicated also by several 40–50 mm. experiments which were allowed to proceed until over 99% of the methyl cyclobutyl ketone should have decomposed at 390–400°. The ratio of the final pressure to the initial pressure was found to be 2.0, but in view of the slow subsequent reactions of the primary products the agreement between the value of P_f/P_0 and 2 is somewhat fortuitous.

Results and Discussion

Pressure–Time Curve and Homogeneity.—By pressure measurements it was observed that the decomposition proceeds without an induction period with the slope of the pressure–time curve decreasing with time as expected for a first-order reaction. To determine whether the decomposition of methyl cyclobutyl ketone is homogeneous, experiments were performed in the packed reaction vessel with a 28-fold greater surface to volume ratio. Eight experiments at initial pressures from 47 to 84 mm. in the packed bulb gave an average quarter-time of 6.8 ± 0.3 min. in comparison with an average value of 7.1 min. for the unpacked vessel. In view of the large increase in the surface to volume ratio these results indicate that more than 99% of the decomposition in the unpacked vessel occurs in the gas phase.

Order of the Reaction.—For the establishment of the order of the reaction several types of evidence were obtained. Experiments were performed at 400° with initial pressures from 10 to 65 mm. As the representative results in Table II indicate, the difference in the quarter-time over the pressure range used does not exceed the experimental variations of the quarter-time in experiments at constant initial pressure. The lack of any significant change in the rate constant over a sixfold change in initial pressure is an indication of a first-order decomposition. The ratio of the half-time to the quarter-time ($t_{1/2}/t_{1/4}$) was measured for a large number of experiments under a variety of conditions including different samples. The average value of the ratio was found to be within 0.01 of the value of 2.41 expected for a first-order reaction. The experimental data obtained during the course of the decomposition were plotted as log $(P_0/(2P_0 - P_t))$ against time where P_0 and P_t are the pressures at the start and at time t. The fact that a linear relationship is observed for at least the first half of the decomposition gives evidence for a first-order reaction. In several experiments the slope of the line was used for the calculation of a value of the first-order rate constant which was compared with the rate constant computed from the quarter-time taken from the pressure–time curve (after dead space correction). The rate constants by the two methods were in satisfactory agreement,

TABLE II

THERMAL DECOMPOSITION OF METHYL CYCLOBUTYL KETONE AT 400.0 ± 0.3°

P_0, mm.	$t_{1/4}$ min.	$10^4 k$, sec.$^{-1}$	Sample[a]	Manometer[b]
10.8	7.2	6.7	D-5	W
24.0	7.1	6.8	B	M
40.1	7.2	6.7	D-2	W
47.2	7.2	6.7	B	M
47.2	7.1	6.8	D-5	W
51.5	7.0	6.8	B	M
56.9	7.1	6.8	D-5a	W
59.0	7.3	6.6	C-4c	M
64.9	6.9	6.9	D-5	W

[a] Sample designations are given in the Experimental section. [b] M denotes the ordinary manometer; W denotes the wide-bore mercury manometer read with a cathetometer.

the average difference being about 1.4%. Normally the latter method was used.

In an attempt to learn more about the behavior of the first-order rate constants with decreasing initial pressures some experiments in the range 1–5 mm. were performed, but the accuracy of the measurements with the apparatus used was not sufficient to provide consistent data at the lower pressures.

Activation Energy.—Experiments were performed over the temperature range 360–410° at approximately 10° intervals with pressures near 10 and 50 mm. In the case of the 50 mm. experiments both the ordinary mercury manometer and the wide-bore manometer (read with a cathetometer) were used for the rate measurements and gave similar results. The data are summarized in Fig. 1 in which logarithm of the first-order rate constant in sec.$^{-1}$ is plotted against the reciprocal of the absolute temperature. The activation energy was evaluated from the slope of best line drawn by inspection and by a least squares analysis of the data. On the basis of the 50 mm. experiments the two methods indicated an activation energy of 54.5 kcal./mole (to the nearest 0.5 kcal.). An activation energy within the range 54.5 ± 0.5 kcal./mole was found also for the rate of appearance of methyl vinyl ketone. Although the results at 10 mm. were not as extensive or as precise as those at 50 mm., the rate constants were usually in agreement with the values at 50 mm. Thus there is no indication of a significant change in the activation energy over the pressure range studied. Likewise the various samples of methyl cyclobutyl ketone gave concordant results.

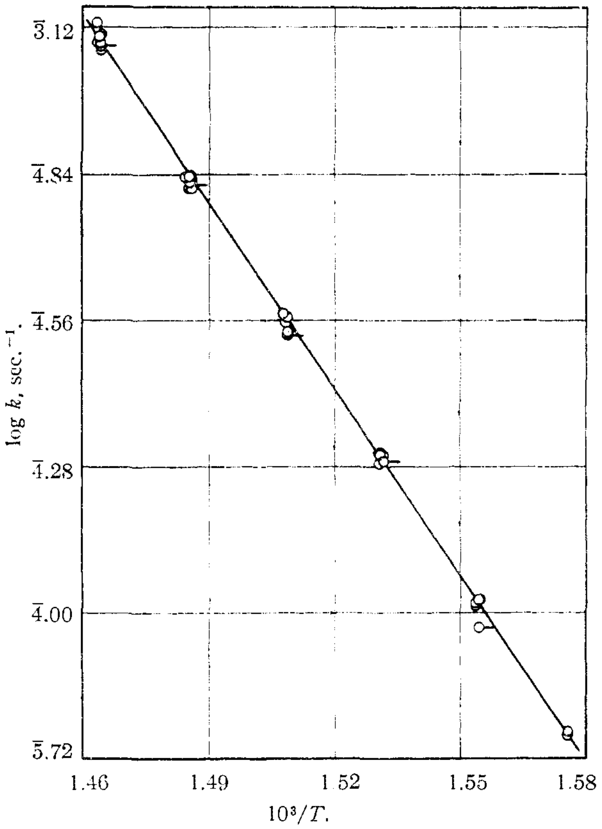

Fig. 1.—Rate of decomposition of methyl cyclobutyl ketone at different temperatures: experiments at ~50 mm. O; ~10 mm., O—. Line drawn on the basis of the 50 mm. experiments.

From the 50 mm. experiments, a rate expression was calculated

$$k = 3.4 \times 10^{14}\, e^{-54500/RT} \text{ sec.}^{-1}$$

Influence of Added Substances.—Since propylene, nitric oxide and toluene have been found to inhibit many free radical chain processes,[3a,17] a number of experiments were performed in the presence of one of these inhibitors. The data from these experiments are summarized in Table III. The values listed in the last column of the table indicate that the time for methyl cyclobutyl ketone to undergo 25% decomposition is not significantly alerted by the addition of nitric oxide, propylene or toluene. Moreover, the shapes of the pressure–time curves with and without the added substance were essentially the same.

TABLE III

EFFECT OF ADDED SUBSTANCES UPON THE THERMAL DECOMPOSITION OF METHYL CYCLOBUTYL KETONE AT 400°

P_0,[a] mm.	Added substance	$P_{A.S.}$,[a] mm.	$t_{1/4}$ min.
40–65	....	..	7.1[b]
50.6	Nitric oxide	0.7	7.0
47.0	Nitric oxide	1.3	7.0
46.8	Nitric oxide	2.5	7.2
46.9	Nitric oxide	2.5	7.2
49.4	Propylene	17.8[c]	7.0
48.3	Propylene	26.7	7.1
49.3	Propylene	38.1	7.7
47.7	Toluene	25.9	7.0
47.7	Toluene	24.9	7.4

[a] P_0 is the initial pressure of methyl cyclobutyl ketone and $P_{A.S.}$ is the pressure of the added substance. [b] Average of 22 experiments. [c] Propylene added after 2.5 min.

Discussion

On the basis of the type of ring cleavage and the first-order character observed for the thermal decomposition of methyl cyclobutyl ketone it appears that the reaction resembles the thermal decompositions of cyclobutane and other four-membered carbocyclic compounds. Although a free radical chain mechanism could be written to explain the observed products, the lack of inhibition in the presence of added propylene or toluene indicates that the decomposition does not take place to an appreciable extent by radical chain processes. The occurrence of a single reaction (ring cleavage) in the thermal decomposition is in contrast to the photolysis of methyl cyclobutyl ketone where the breaking of the C–C bonds adjacent to the carbonyl group gives free radicals that undergo secondary reactions yielding a larger number of products.[7] Moreover, the thermal decomposition of methyl cyclobutyl ketone is considerably different from the pyrolysis of methyl *n*-butyl ketone which

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[17] L. A. K. Staveley and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **154A**, 335 (1936); M. Szwarc, *J. Chem. Phys.*, **17**, 431 (1949). For the decompositions of certain ketones nitric oxide is not a satisfactory inhibitor. See references 3b-e.

results in the formation of a variety of products mainly as a result of free radical chain reactions.[3e]

From the available evidence it seems that the thermal decomposition of methyl cyclobutyl ketone may be a unimolecular reaction. Since no significant fall-off in the rate constant was detected at 10 mm., the pressure region of the fall-off appears to be below that of cyclobutane[4] as might be anticipated for a molecule with a greater number of vibrational degrees of freedom. The frequency factor for the decomposition lies within the limits expected for a unimolecular reaction. The frequency factor A of a unimolecular gas reaction can be expressed as

$$A = \kappa e(kT/h)e^{\Delta S^{\ddagger}/R}$$

where κ is the transmission coefficient and $\Delta S^{\ddagger}$ is the entropy of activation.[18] From the experimental value of the frequency factor and with the assumption that the transmission coefficient is unity, one can calculate that the entropy of activation at 400° is +4.3 cal./deg. mole. A positive value would be expected for a reaction involving the cleavage of the ring.

In comparison with the thermal decompositions of cyclobutane[4] and ethylcyclobutane[5] the activation energy for the decomposition of methyl cyclobutyl ketone is 7.5–8.0 kcal./mole lower. Although this decrease in activation energy is partially compensated by a lower frequency factor (smaller apparent entropy of activation), the methyl cyclobutyl ketone decomposition takes place at temperatures approximately 50° lower than the decompositions of ethylcyclobutane and cyclobutane (for similar rates). In this connection it is to be noted that the product methyl vinyl ketone possesses some resonance energy which would not be associated with the corresponding product in the decomposition of ethylcyclobutane or cyclobutane. The effect of resonance in the product may result in some lowering of the activation energy if the decomposition proceeds by a direct formation of methyl vinyl ketone and ethylene. As an indication of the resonance energy of methyl vinyl ketone, there is the value of the resonance energy for crotonaldehyde which was reported to be 2.9 kcal./mole.[19] On the basis of certain corrections for polar and hyperconjugation effects[20] a higher value (7.3 kcal./mole) has been suggested recently. If the rate-determining step in the decomposition involves the formation of a biradical (by the breaking of the ring C–C bond nearest the carbonyl group), there should be more resonance in the biradical formed from methyl cyclobutyl ketone than in the corresponding biradical from an alkyl derivative of cyclobutane. The presence of any resonance in the biradical should lower somewhat the activation energy of the formation of the biradical from methyl cyclobutyl ketone. In the comparison of the present results with those from the decompositions of other four-membered ring compounds it was observed that the frequency factor and the activation energy for methyl cyclobutyl ketone are much closer to those of cyclobutanone ($k = 3.6 \times 10^{14}\ e^{-52000/RT}$ sec.$^{-1}$) than to those of ethylcyclobutane or cyclobutane.

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[18] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 295.

[19] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith and W. E. Vaughan, THIS JOURNAL, **60**, 440 (1938).

[20] M. M. Kreevoy and R. W. Taft, Jr., *ibid.*, **79**, 4016 (1957).

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE A. AND M. COLLEGE OF TEXAS]

Quantitative Relationship between Structure and Reactivity for the Reactions between Diphenyldiazomethanes and Benzoic Acids in Toluene at 25°

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Rate constants at 25° have been determined for the reaction of diphenyldiazomethane (DDM) with twelve *m*- or *p*-substituted benzoic acids (XBA's) in toluene. Correlation analysis of the data yields eq. 2: $\log k_2 = -0.1023 + 2.513\Sigma\sigma_B$ with $r = 0.9947$ and $s = 0.0913$. In a previous article,[1] correlation analysis of the data for the reaction of benzoic acid (BA) with twelve *m*- and/or *p*-substituted diphenyldiazomethanes (XDDM's) yielded eq. 1: $\log k_2 = -0.1440 - 1.570\Sigma\sigma_D$ with $r = 0.9987$ and $s = 0.0442$. If the structures of both reactants are varied simultaneously and the two effects are independent, it appears that the resulting data would be closely represented by eq. 4: $\log k_2 = -0.1231 - 1.570\Sigma\sigma_D + 2.513\Sigma\sigma_B$ where -0.1231 is the average of the intercepts from eq. 1 and 2, -1.570 and $+2.513$ are ρ_D and ρ_B from eq. 1 and 2, and $\Sigma\sigma_D$ and $\Sigma\sigma_B$ are the summations of σ-values in the XDDM and in the XBA. Rate constants at 25° have been determined for twenty-one reactions of XDDM's with XBA's in toluene. For these reactions plus two others from ref. 6, substitution of $\Sigma\sigma_D$ and $\Sigma\sigma_B$ values into eq. 4 yields calculated $\log k_2$ values which show an average deviation of 0.084 from experimental $\log k_2$ values. For the forty-six available reactions of XDDM's or DDM with XBA's or BA, the analysis of the multiple regression yields eq. 5: $\log k_2 = -0.1089 - 1.620\Sigma\sigma_D + 2.376\Sigma\sigma_B$ with $R = 0.9975$ and $s = 0.0783$. The very close fit of eq. 5 offers conclusive evidence that the effect of *m*- and/or *p*-substituents on the DDM is independent of the effect of *m*- or *p*-substituents on the BA.

Introduction

For the reaction at 25° in toluene of benzoic acid (BA) with diphenyldiazomethane (DDM) and with eleven *m*- and/or *p*-substituted diphenyldiazomethanes (XDDM's), it has been shown[1] that

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[1] C. K. Hancock, R. F. Gilby, Jr., and J. S. Westmoreland, THIS JOURNAL, **79**, 1917 (1957).