scattered light trace and the recombination trace is proportional to the iodine atom concentration. The precision of these results was less than for those in the gas phase[9,14] because of the smaller per cent. initial dissociation, resulting from the caging effect, and the faster rate of recombination, resulting from the constant presence of solvent molecules to serve as the "third body." Nevertheless, the best curve through the $1/[I]$ *vs.* time plot clearly showed a second-order dependence of the rate on the iodine atom concentration. Values of k in the relation $d[I_2]/dt = k[I]^2$ were calculated as previously described[9,14] and are given in Table II for 20 determinations. Included in the table are the values obtained for the iodine atom concentration at 150 microseconds, which were used in the calculation of the primary quantum yield.

TABLE II

RECOMBINATION RATE CONSTANTS FOR IODINE IN CARBON TETRACHLORIDE AT ROOM TEMPERATURE

$[I_2]_0 = 1.84 \times 10^{-5}$ mole/liter

$k \times 10^{-9}$, l. mole^{-1} sec.$^{-1}$	$[I] \times 10^7$ at t = 150 μsec. mole/l.	$k \times 10^{-9}$, l. mole^{-1} sec.$^{-1}$	$[I] \times 10^7$ at t = 150 μsec. mole/l.
5.16	7.6	5.96	9.7
5.48	9.0	5.96	9.7
6.30	10.2	5.31	8.8
5.74	10.3	6.66	9.5
6.71	9.8	5.27	8.5
5.86	8.8	5.11	9.4
5.40	9.7	6.47	8.3
5.96	11.0	5.27	9.0
5.10	7.7	5.39	9.1
5.96	9.7	5.39	9.5

Av. of k values = $5.7 \pm 0.5 \times 10^9$ l. mole^{-1} sec^{-1}.

Discussion

The procedures outlined above gave a value of 0.13 for the fraction of the iodine molecules in carbon tetrachloride solution which, having absorbed a photon, produce iodine atoms which escape recombination to the parent partnership. The light used was the full light of the xenon flash lamp transmitted by a Pyrex cell.

Marshall and Davidson,[7] also using the flash technique, but making no attempt to correct quantitatively for the time dependence of the flash intensity or for the difference in the absorption spectra of iodine in the gas and in solution, and using only light of wave lengths greater than 5000 Å., obtained 0.19 molecule dissociated per quantum. From a determination of the quantum yield for disappearance of iodine in air-saturated solutions of allyl iodide in carbon tetrachloride solution, Lampe and Noyes[8] have obtained a value of 0.14 for the quantum yield of I atom escape from the parent partnership. This determination was made with 4368 Å. light. It is presumed that the allyl iodide reacts with all of the iodine atoms which escape recombination and that the radicals so formed are removed from further chemical activity by reaction with oxygen.

The fact that three laboratories using two widely different techniques obtain values as close together as those cited above is convincing evidence that the true value lies in the region indicated. It, together with the values which have been obtained for iodine in hexane[7,8] (0.41, 0.66) and in hexachlorobutadiene[9] (0.075), offers the most direct experimental evidence yet obtained for the "cage effect."[3] It will be desirable if it is possible for the direct measurements by the flash photolysis technique to be extended to determine the effect of wave length and of a variety of solvents. Use of the analog computer technique described in this paper makes quantitative determinations of this type possible even when the duration of the flash is necessarily appreciable relative to the time required for atom recombination.

Acknowledgment.—This work was supported in part by the United States Atomic Energy Commission, and by the University Research Committee with funds made available by the Wisconsin Alumni Research Foundation. It also was aided by fellowships supported by the United States Rubber Co. and the Minnesota Mining and Manufacturing Co.

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

The Thermal Decomposition of Methyl *n*-Butyl Ketone[1,2]

BY WILLIAM T. BARRY, JR., AND W. D. WALTERS

RECEIVED DECEMBER 13, 1956

The gas-phase thermal decomposition of methyl *n*-butyl ketone has been studied in the neighborhood of 430–500°. The principal products of the reaction during the early stages are: (a) propylene and acetone, (b) ethane and methyl vinyl ketone and (c) methane, carbon monoxide and 1-butene. A small quantity of ethylene also has been found. Acid-forming constituents, *e.g.*, ketenes, are present in only small amounts. The order of the decomposition is about 1.3 and the variation of the rate with temperature gives an apparent activation energy of approximately 52 ± 3 kcal./mole for 200 mm. experiments. The reaction is predominantly homogeneous although it is inhibited to a slight extent by packing the reaction vessel. The addition of propylene markedly inhibits the decomposition. Small quantities of added biacetyl at 475° or ethylene oxide at 450° accelerate the decomposition.

The thermal decomposition of methyl *n*-butyl ketone over a copper–aluminum oxide catalyst has been reported by Mailhe.[3] The composition of the gaseous products was found to be carbon monoxide (18.9%), hydrogen (8.0%), methane (23.5%), saturated hydrocarbons (16.5%) and

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[1] This work was supported by the Office of Naval Research.

[2] Abstracted from the Ph.D. thesis submitted by William T. Barry, Jr.

[3] A. Mailhe, *Bull. soc. chem. France*, **31**, 863 (1922).

unsaturated hydrocarbons (33%). The unsaturated fraction consisted of ethylene, propylene and 1-butene. A liquid product fraction boiling below 90° was obtained, but not identified. The photolysis of methyl *n*-butyl ketone has been studied rather extensively[4] and the chief products at low temperatures are acetone and propylene. Davis and Noyes[4b] found that the acetone yield is relatively constant under all conditions indicating that acetone and propylene are formed in a single step. It was of interest to investigate the homogeneous thermal decomposition in order to make a comparison with the photochemical studies and with the thermal decompositions of the lower ketones.

Experimental

Materials and Apparatus.—Methyl *n*-butyl ketone was prepared in this Laboratory (a) by the reaction[5] of *n*-butylmagnesium bromide with an excess of acetic anhydride at −70° and (b) by converting *n*-butylmagnesium bromide to the cadmium alkyl with anhydrous cadmium chloride and treating the cadmium alkyl with acetyl chloride.[6] Methyl *n*-butyl ketone (c) which had been prepared by the chromic acid oxidation of 2-hexanol was purchased from Paul C. Kletzke Co.

Materials (a) and (b) were purified by recrystallization of the semicarbazone and the regenerated samples of the ketone (aI and bI) were dried over anhydrous calcium sulfate, filtered and fractionated. In one instance, material (a) was purified by conversion to the bisulfite addition compound and regeneration of the ketone gave sample (aII). Material (c) was shaken with pure mercury for 24 hours to remove peroxides, distilled once, and then fractionated. All of the samples were fractionated (usually twice) in an atmosphere of pure, dry nitrogen. Similar results were obtained with the various samples described above. The indices of refraction of the purified samples were: n^{24}D for sample (aI) 1.3991; n^{20}D for (bI) 1.4006, (aII) 1.4009, and (c) 1.4006. A value of 1.4008 for n^{20}D has been reported previously.[7]

Ethylene oxide was obtained from the Dow Chemical Co. Biacetyl from the Eastman Kodak Co. was purified by fractionation under vacuum. Propylene (99.5%, Ohio) was used without further purification other than thorough degassing at −196°. Nitrogen (99.99%) was supplied by Linde Air Products Co. Nitric oxide (Matheson) was passed through three traps at −160°, and before each use it was frozen at −196°, degassed and distilled from a −78° bath.

The apparatus was almost identical with the one used in an earlier study.[8] The rate of pressure rise was measured usually with a heated mercury manometer, but in some experiments a click gage or a mirror gage was used.

Analysis of the Products.—Infrared measurements, conventional gas analysis involving absorption and combustion techniques and mass spectrometric analyses[9] were used to identify the gaseous products. To establish the identity of butene the more volatile products from a series of static experiments were removed by vaporization at low temperatures; the infrared absorption curve for the less volatile portion of the gases indicated that the main C_4 hydrocarbon is 1-butene. Prior to the quantitative analyses the gaseous products were separated usually into a fraction volatile at −196° and another volatile at −78°.

Tests for formaldehyde[10] and for higher homologs[11] did not reveal the presence of any aldehyde. A solution of the products in water showed a slight acid reaction, indicating the presence of ketene, substituted ketenes or other acidic substances. By titration with standard base it was found that after 10–20% pressure increase at 450° for 250 mm. experiments ketenes are present to the extent of less than 1% of the gaseous products. For an initial pressure of about 120 mm. at 512° with a pressure increase of 58–64% the acidic constituents amounted to 3.4% of the gaseous products.

In order to secure sufficient amounts of the liquid products for identification a series of static experiments (250–300 mm., 525°, 40–75% pressure increase) was performed. The liquid portion of the reaction mixture was fractionated in a semi-micro column. The boiling point and the index of refraction were measured for each fraction. Since the evidence indicated the presence of acetone and methyl vinyl ketone as important products (formed in comparable amounts), the semicarbazones of the appropriate fractions were prepared, recrystallized and compared with the semicarbazones from the pure ketones. The data are summarized in Table I. The infrared curves of fraction I4 and I8 agreed with the curves for acetone and methyl vinyl ketone, respectively. There appeared to be a trace of acetone in I8. Some evidence was obtained for the presence of another substance which came over in the first fraction of the distillation along with 1-butene and acetone. It had a maximum in its ultraviolet absorption at 223 mμ, but due to the minute quantity an infrared identification could not be made.

TABLE I

Fraction	B.p., °C.	n^{20}D	M.p., °C. Semicarbazone	M.p., °C. Mixed
I4	55.8[a]	1.3610	184–188	184–187
I8	80[a]	1.4096	140–144	141–143
Acetone	56.2[b]	1.3591[b]	184–187	
Methyl vinyl ketone	81[c]	1.4095[c]	141–143	

[a] 744 mm. [b] From reference 12a, b.p. at 760 mm. [c] From reference 12b, refractive index at 22°.

The amount of methyl vinyl ketone in the products was determined by two methods. The products which had not volatilized at −78° were dissolved in a 0.1 *N* potassium chloride solution (90% water–10% methanol). A portion of this solution was used for polarographic measurements[13] carried out with a Fisher Elecdropode. A second portion of the solution was diluted with water and the optical density was determined at 210 mμ with a Beckman DU spectrophotometer. For each method standard solutions of methyl vinyl ketone were used for calibration purposes.

Acetone in the products was estimated by a colorimetric method involving the reaction with vanillin.[14] A wave length of 540 mμ was employed and the contributions resulting from the methyl vinyl ketone and the unreacted methyl *n*-butyl ketone were taken into account. The acetone analyses seemed to be satisfactory for a comparison between experiments on a relative basis, but the absolute values may have been in error by 20–25%.

Results

Products of the Reaction.—The results from the mass spectrometric analyses of the gaseous products formed at 450 and 475° are plotted in Fig. 1. The data from two other series of experiments analyzed by conventional gas analytical procedures were in good agreement with those shown in Fig. 1. In the initial stages of the decomposition propylene and ethane are the most important gaseous products. For comparison a plot of (pressure of methyl vinyl ketone/pressure of gaseous products) for a

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(11) L. Lewin, *Ber.*, **32**, 3388 (1899).

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(14) H. L. J. Backstrom, *Z. anal. Chem.*, **123**, 96 (1941).

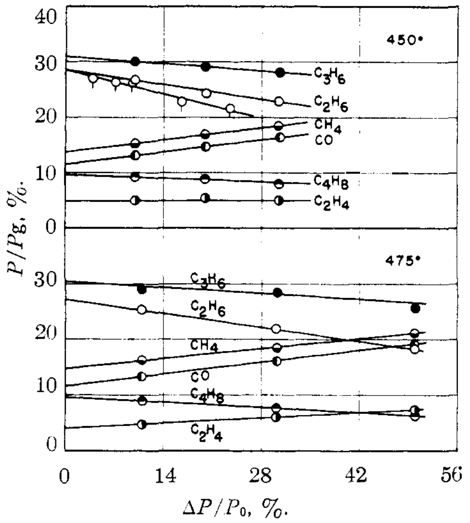

Fig. 1.—Products formed during the decomposition of methyl *n*-butyl ketone, 250 mm. at 450° and 160 mm. at 475°. P/Pg represents the ratio of the amount of each substance to the total amount of gaseous products in % for various percentages of pressure increase ($\Delta P/P_0$, %). ♀ gives the ratio of methyl vinyl ketone to gaseous products for experiments at 200 mm.

series of 200 mm. experiments at 450° is shown also in Fig. 1. The agreement between the ethane and methyl vinyl ketone at the start of the decomposition indicates that one of the reactions is

$$CH_3COC_4H_9 \longrightarrow CH_3COCH{=}CH_2 + C_2H_6 \quad (1)$$

The acetone determined for 200 mm. experiments at 450° by the colorimetric method appeared to be about 80–85% of the percentage of propylene shown in Fig. 1. In view of the difficulties inherent in the colorimetric method in the presence of other ketones the results point toward the occurrence of

$$CH_3COC_4H_9 \longrightarrow CH_2{=}CHCH_3 + CH_3COCH_3 \quad (2)$$

The fact that the lines for methane, carbon monoxide and butene extrapolate to percentages of comparable magnitudes at the beginning of the reaction gives evidence for the reaction

$$CH_3COC_4H_9 \longrightarrow C_4H_8 + CH_4 + CO \quad (3)$$

Since methane and carbon monoxide grow in importance during the decomposition, they are probably formed also by the decomposition of intermediate products. It might be expected that in the presence of undecomposed ketone and liquid products some of the butene may remain in the −78° trap. Two experiments employing a more elaborate procedure of separation by fractional condensation and volatilization indicated that as much as eight parts per hundred of the butene might have been retained, but the loss of other gases was negligible. Thus the amount of butene may be somewhat closer to the carbon monoxide than the data in Fig. 1 show.

The presence of ethylene in the initial portion of the decomposition points toward the occurrence of at least one other reaction of lesser importance, as will be considered in the Discussion. For the experiments at 450 and 475° other products not shown in Fig. 1 were found in the gases by the mass spectrometric analyses: H_2, 0.3–0.8%; C_3H_8, 0.2–1.7%; C_5-C_6 hydrocarbons, 0.1–0.3%; CH_3COCH_3, 0.2–0.4% (most of the acetone is in the condensed fraction).

It was observed that the relative proportions of the products change as the decomposition proceeds, but for a given percentage of pressure increase the composition, particularly in the early stages, does not depend appreciably upon the initial pressure or temperature over the range used in this study. This finding indicated that the pressure increase could be used for the investigation of the kinetics of the reaction.

To study the appearance of methyl vinyl ketone during the decomposition both the spectrophotometric and the polarographic methods were used and the data are summarized in Fig. 2. The pressure of methyl vinyl ketone rises rapidly at first, reaches a maximum and then gradually diminishes in the later stages of the decomposition. In the early portion the points representing the polarographic and spectrophotometric measurements are essentially coincident, but at the higher percentages of pressure increase ($\Delta P/P_0$) where the reaction times are considerably longer, there are differences probably due to the ultraviolet absorptions of secondary products.

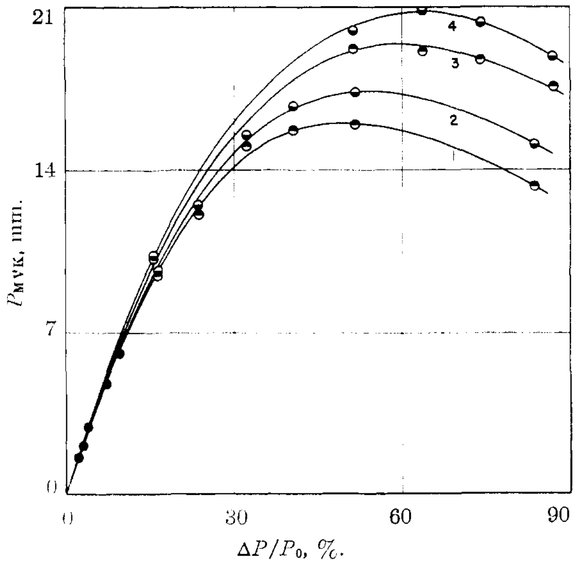

Fig. 2.—Methyl vinyl ketone present during the decomposition of methyl *n*-butyl ketone: Curves 1 and 2, ~200 mm. of $C_6H_{12}O$ at 450°; curves 3 and 4, ~198 mm. of $C_6H_{12}O$ at 495°. Pressure of methyl vinyl ketone based on polarographic measurements, ◓; on the ultraviolet absorption of a solution of the reaction mixture at 210 mμ, ◒.

Pressure–Time Curve and Homogeneity.—The change of pressure with time at 450° is shown in curve 1, Fig. 3. The slope of the curve decreases more than expected during the first ten minutes and then remains almost constant to about 60% pressure increase. The decrease in the initial stages may be due to the formation of products, such as propylene, which can inhibit the reaction. Later, secondary reactions involving the products initially formed will be occurring.

Curve 2 in Fig. 3 shows that a 22-fold increase in the surface to volume ratio reduces the rate of pressure rise. This decrease may result from the increase in the termination of free radical chains due to packing. Analyses after 40 min. at 450° showed that methyl vinyl ketone in the packed vessel is about 90% of that in the unpacked vessel for similar experiments at 200 mm. In view of the large difference in the total surface between the packed and unpacked vessels it is probable that surface effects play a relatively insignificant role in the unpacked bulb under the conditions used.

Influence of Added Substances.—The effect of the addition of propylene upon the rate of pressure rise is shown in curve 3, Figure 3. It was observed that as little as 4 mm. produces some decrease in the initial rate and the addition of 150 mm. propylene inhibits about 80% or more of the initial rate of pressure increase. Analyses were performed in order to ascertain whether this decrease in the rate of pressure rise is associated with a real inhibition of the decomposition. The amounts of methyl vinyl ketone present at 475° with and without added propylene are shown in Table II.

TABLE II

EFFECT OF PROPYLENE UPON THE APPEARANCE OF METHYL VINYL KETONE AT 475°

Propylene added, mm.	0	150	200	250
Reaction time, min.	Methyl vinyl ketone present, mm.			
2.5	3.2	0.75	0.67	0.49
11.5	9.8	3.9	3.5	3.1

P_0 (methyl *n*-butyl ketone) = 200 ± 4 mm.

A similar inhibiting effect of propylene upon the build-up of methyl vinyl ketone was observed at 450°. The results show that the major portion of the methyl vinyl ketone is formed by a chain process which is markedly inhibited by propylene. It is to be noted that the addition of 100 mm. of nitrogen to 200 mm. of methyl *n*-butyl ketone at 450° produced no appreciable effect upon the pressure–time curve or upon the amounts of methyl vinyl ketone and acetone formed in 40 min.

To find out whether the formation of other products is affected by propylene, gas analyses were made on reaction mixtures from experiments in the presence of propylene and the quantities of products were compared with the quantities from pure methyl *n*-butyl ketone under similar conditions (Table III). It is apparent from these results that the processes producing carbon monoxide and methane are inhibited by propylene. Since ethane is the principal higher saturated hydrocarbon, the formation of ethane is presumably decreased also.

TABLE III

AMOUNTS OF PRODUCTS FORMED WITH ADDED PROPYLENE RELATIVE TO THE AMOUNTS FROM PURE METHYL *n*-BUTYL KETONE (200 MM.) AT 450°

Reaction time, 40 min.

Propylene, mm.	$\Delta P_i/\Delta P_n$[a]	CO	CH_4	Higher saturates	Unsaturates
80	0.45[a]	0.38	0.45	0.52	0.3
160	.38[a]	.38	.42	.50	.4

[a] Ratio of the pressure increases in the presence and absence of propylene.

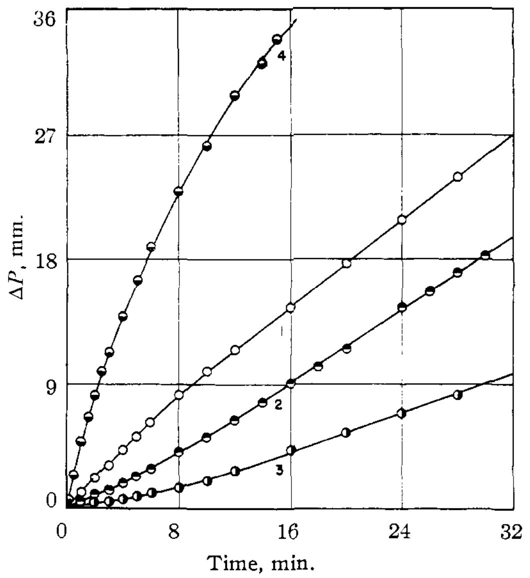

Fig. 3.—Pressure increase during the decomposition of 200 mm. of methyl *n*-butyl ketone at 450°: ○, pure ketone; ◓, packed bulb (other curves from unpacked bulb); ◑, 105 mm. of propylene added; ◒, 1% ethylene oxide and 99% ketone.

The values for the unsaturates are subject to considerable error since they were obtained by subtraction of the amount of added propylene, but the rate of production of olefins seems definitely lower in the presence of propylene.

The effect of propylene upon the formation of acetone was evaluated semi-quantitatively in two ways. The colorimetric method was used for (a) two experiments with 200 mm. of methyl *n*-butyl ketone at 475° for 2.5 min. with 151 and 201 mm. of added propylene and (b) the experiments shown in Table III (greater percentages of decomposition and smaller pressures of propylene). It was estimated that the acetone in the presence of propylene compared to that in the normal decomposition probably does not exceed a value of 15% in the case of the (a) experiments and is not greater than 45% for the experiments shown in Table III. The infrared absorption technique was employed for experiments with 200 mm. of methyl *n*-butyl ketone in the presence and absence of 260 mm. of propylene for reaction times of 40 and 56 min. at 450°. In each case a sample of vapor removed from the liquid portion of the reaction mixture by volatilization was examined in the region of 8.2μ where acetone absorbs quite strongly and the absorptions of methyl vinyl ketone and methyl *n*-butyl ketone are relatively weak. The absorption observed for acetone (after correction for the absorption of methyl *n*-butyl ketone) in the inhibited experiments seemed to be not more than 30–35% of the absorption of samples for the experiments without added propylene. On the basis of these results it can be concluded that the added propylene under the above conditions inhibits at least 60% of the acetone formation.

Experiments with 0.3–7.0 mm. of nitric oxide added to 200 mm. of methyl *n*-butyl ketone at 450° gave a decrease in the time for 10% pressure increase rather than an inhibition of the rate of pressure rise.

Addition of 1% biacetyl to 200 mm. of methyl *n*-butyl ketone at 475° accelerated the decomposition, the increase in total pressure after 9.5 min. being 1.06 times as great as that after 18 min. ($\Delta P/P_0$ = 24%) in the normal decomposition. From the analyses the ratio of the amount of each product formed in the 9.5 min. accelerated decomposition to the amount formed in 18 min. without added biacetyl was found to be: CO, 1.17; CH_4, 1.1; higher saturates, 1.0; C_2H_4, 1.1; higher unsaturates, 0.97; methyl vinyl ketone, 1.1. The product ratios are very close to the ratio of the over-all pressure increases for the two conditions. From these observations it is evident that the products formed in the biacetyl promoted decomposition are in similar proportion to that found in the normal decomposition. The slight excess of carbon monoxide probably comes from the added biacetyl which has decomposed.

Other experiments showed that radicals from decomposing ethylene oxide can sensitize the decomposition. The influence of added ethylene oxide is shown in curve 4, Fig. 3. For a 200 mm. mixture of methyl *n*-butyl ketone and 1% ethylene oxide the increase in the total pressure at 450° after 15 min. was 1.03 times as large as that observed for 200 mm. pure ketone in 40 min. ($\Delta P/P_0$ = 16.5%). Ratios of the amounts of the products formed in the 15 min. sensitized decomposition to those in the 40 min. normal decomposition were: CO, 1.1; CH_4, 1.16; higher saturates, 1.0; C_2H_4, 1.1; higher unsaturates, 1.1; methyl vinyl ketone, 1.0. The ratio is approximately the same for every product and is close to the value of 1.03 for the ratio of the observed pressure increases. These results also give evidence for the similarity of the products in the normal and sensitized decompositions.

Kinetics.—In experiments at 450° with pressures from 50 to 300 mm. the initial slope of the pressure–time curve $(dP/dt)_0$ and the rate of pressure rise in the region of essentially constant slope (after 6% pressure increase at 450°) were measured and their logarithms were plotted against the logarithm of the initial pressure (Fig. 4). Likewise the average rate of build-up of metal vinyl ketone during the first 8 min. $(\Delta P_{MVK}/\Delta t)$ was measured and the data are shown in Fig. 4. The slopes of the three lines are almost the same and all lie within the range 1.30 ± 0.06. Thus an order of about 1.3 is indicated for the over-all reaction and for the build-up of methyl vinyl ketone.

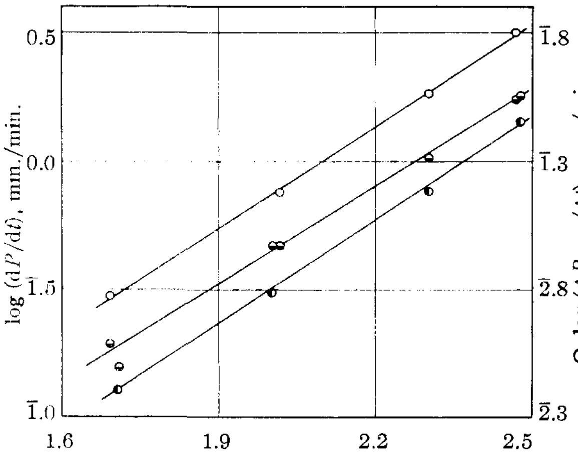

Fig. 4.—Change in rate with initial pressure, P_0: ◒, $(dp/dt)_0$, initial rate of pressure rise; ◐, $(dp/dt)_c$, rate of pressure rise after ∼6% pressure increase; O, $(\Delta P_{MVK}/\Delta t)$, average rate of build-up of methyl vinyl ketone during the first 8 min. Each point showing the rate of pressure rise at 200 mm. represents the average of three values.

Figure 5 summarizes the data showing the temperature variation of the reaction over the range 430–495° at a constant pressure of 200 ± 2 mm. (or corrected to this value). Each point in Fig. 5 represents two or more experiments. For methyl vinyl ketone in Figs. 4 and 5, each point is the average of the spectrophotometric and polarographic analyses, the former being on the average about 5% higher. If one assumes that for a constant initial pressure each of the rates can be represented by an expression involving a constant multiplied by $e^{-E/RT}$, the values for E obtained from the data shown in Fig. 5 are: 50 ± 2 kcal./mole from $(dP/dt)_0$, 52 ± 1 kcal./mole from $(dP/dt)_c$, and 53.5 ± 1 kcal./mole from $(\Delta P_{MVK}/\Delta t)$. It is to be noted that for the measurement of $(\Delta P_{MVK}/\Delta t)$ the reaction time at each temperature was kept sufficiently short to permit the build-up of only 2.7-3.1 mm. of methyl vinyl ketone. Due to secondary reactions the observed rate of build-up will not be identical with the rate of formation, but the difference should be small. In the evaluation of the temperature variation and the order by the use of $(\Delta P_{MVK}/\Delta t)$ a compensating factor is that approximately similar percentages of methyl vinyl ketone may disappear in the various experiments.

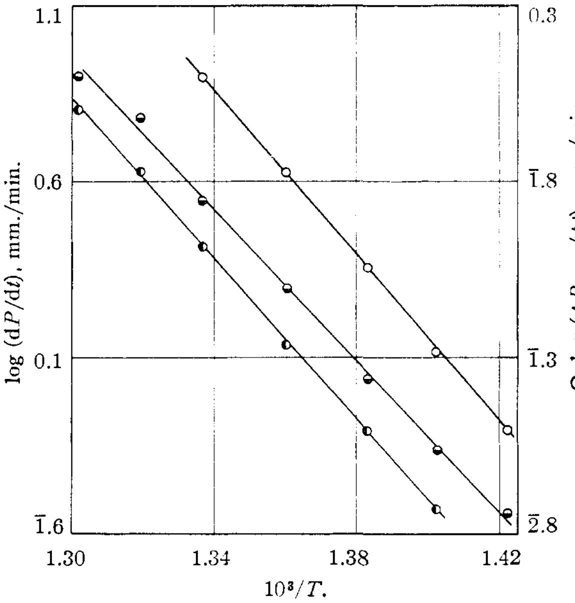

Fig. 5.—Variation of rate with temperature: ◒, $(dP/dt)_0$, initial rate of pressure rise; ◐, $(dP/dt)_c$, rate of pressure rise after ∼10% pressure increase; O, $(\Delta P_{MVK}/\Delta t)$ initial rate of appearance of methyl vinyl ketone.

To estimate the importance of the disappearance of methyl vinyl ketone for the kinetic studies above, two experiments with 11 mm. of this compound plus 200 mm. nitrogen were allowed to proceed for 8 min. at 450°. Analyses did not reveal any significant loss, but the disappearance of about 5% might have escaped detection. Small amounts (12 mm.) of methyl vinyl ketone were added to 200 mm. of methyl *n*-butyl ketone and analyses were made after 8, 24 and 40 min. at 450°. The influence of added methyl vinyl ketone upon its own formation is not known, but it is estimated that the disappearance of methyl vinyl ketone probably is not in excess of 1% per minute in the initial stages of the reaction.

Discussion.—The experimental results indicate that even in the initial stages the homogeneous thermal decomposition of methyl *n*-butyl ketone is not a simple reaction, but involves three major reactions designated above as (1), (2) and (3). However, the order and the temperature coefficient of the reaction producing methyl vinyl ketone are approximately the same as the order and temperature coefficient obtained from the rate of pressure increase. Furthermore it has been shown that the three reactions given above can be inhibited by propylene and sensitized by free radicals to form the products in nearly the same proportions as in the normal reaction. The rate of pressure rise is also reduced by an increase in the surface to volume ratio of the reaction vessel. To explain the results a free radical chain mechanism of the Rice–Herzfeld type can be used. Although the exact nature of the primary radical producing process is not known, the rupture of any carbon–carbon bond in methyl *n*-butyl ketone can produce free radicals. The abstraction of a hydrogen atom from the ketone by a radical can then lead to a chain reaction

$$R + CH_3COCH_2CH_2CH_2CH_3 \longrightarrow RH + C_6H_{11}O$$

$$C_6H_{11}O \longrightarrow M + R'$$

$$R' \left(\begin{matrix}\text{or smaller}\\ \text{radical}\end{matrix}\right) + C_6H_{12}O \longrightarrow R'H + C_6H_{11}O$$

The formulas for M and R′ will depend upon the particular hydrogen atom abstracted. In some cases R′ will decompose before abstracting a hydrogen atom. The chain products which could be formed by the type of mechanism given above are shown in Table IV.

TABLE IV

Carbon atom from which H is abstracted	M	Products from reaction of R	
3	$CH_3COCH{=}CH_2$	C_2H_6	(A)
4	$CH_2{=}CHCH_2CH_3$	$CH_4 + CO$	(B)
5	$CH_2{=}CHCH_3$	CH_3COCH_3	(C)
1	$CH_2{=}CO$	$C_2H_4 + C_2H_6$	(D)
6	C_2H_4	$C_2H_4 + CH_4 + CO$	(E)

It is apparent that processes (A), (B) and (C) lead to the formation of the major products. Reactions (A), (B) and (C) would be expected to be important on the basis of the fact that they involve the abstraction of secondary hydrogen atoms and in the case of (A) the hydrogen is on a carbon atom adjacent to a carbonyl group.[15] After the abstraction of hydrogen there are in certain cases alternative routes by which other products might be formed instead of those given in Table IV, but from theoretical considerations or experimental evidence they appear less likely. For example, an alternative to methyl vinyl ketone and ethane in (A) might be propyl ketene and methane, but the experimental results have given no positive evidence for the presence of propyl ketene in important amounts.

That the decomposition of the radical $CH_2COCH_2CH_2CH_2CH_3$ (reaction (D)) does not contribute to a large extent to the formation of the products is indicated by the smallness of the quantities of the ketenes found. Moreover, some of the ketene may be coming from the acetonyl radical (or acetone) formed in reaction (C). The apparent unimportance of process (D) is somewhat surprising since the abstraction of a hydrogen atom from carbon 1 which is adjacent to a carbonyl might be expected to occur to a greater extent.[15a] From a spatial model of the radical it can be seen that there is a position in which carbon atom 1 is close to the hydrogens on carbon 5 so that it may be possible for $CH_2COCH_2CH_2CH_2CH_3$ to isomerize by an intramolecular hydrogen abstraction to $CH_3COCH_2CH_2CHCH_3$.[16] Decomposition of the latter radical would lead to an enhancement of reaction (C) at the expense of reaction (D) and would tend to make the products from (C) more important than (B) as is observed experimentally.

Reaction (E) which produces two molecules of ethylene probably can account for the ethylene formed in addition to that from reaction (D). Since the initial percentage of ethylene is not more than 5% (see Fig. 1), reaction (E), which involves the abstraction of a primary hydrogen atom, does not seem to be as important as (A), (B) or (C).

The decomposition of methyl *n*-butyl ketone appears to have considerable similarity to the decompositions of the lower methyl alkyl ketones particularly with respect to the occurrence of chain processes which are inhibited by propylene.[17] However, with methyl *n*-butyl ketone the reactions leading to the formation of ketenes seem to be less important. The activation energies observed in the present case are close to those (51–53 kcal./mole) found for methyl *n*-propyl ketone.[17d] The order of the reaction of methyl *n*-butyl ketone seems to be somewhat higher than the first order behavior found for the lower ketones; this could be due to the existence of several types of chain termination which might lead to an order between 1 and 1.5.[18]

Although propylene and acetone are among the

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(15) (a) F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," Johns Hopkins Press, Baltimore, Md., 1935, pp. 91 and 108; (b) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1954, p. 499–500; (c) C. N. Hinshelwood, *Disc. Faraday Soc.*, **10**, 266 (1951).

(16) A similar type of isomerization has been suggested by A. Kossiakoff and F. O. Rice, THIS JOURNAL, **65**, 590 (1943), for the 1-hexyl radical.

(17) (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) V. L. Garik, Ph.D. thesis, Univ. of Connecticut, 1953, Univ. Microfilms Pub. No. 6328, Ann Arbor, Mich.

(18) That the chain terminating step is complex in the acetone pyrolysis has been reported by J. R. McNesby, T. W. Davis and A. S. Gordon, THIS JOURNAL, **76**, 823 (1954).

important pyrolytic products from methyl *n*-butyl ketone, in contrast to the photochemical decomposition at low temperatures there are other products formed in comparable amounts. Moreover, the results from the experiments with added inhibitor show that in the thermal decomposition acetone and propylene are formed mainly by a free radical chain process rather than by a single-step reaction.

A detailed treatment of the kinetics of a free radical mechanism has not been attempted on account of the complexity of the chain decomposition which probably involves the participation of a number of different radicals. The inhibiting effect of propylene indicates that even in the relatively early stages of the decomposition a partial inhibition of the reaction by the products should be taken into account. In the later stages the subsequent reaction of several of the primary products would be expected to introduce additional complicating factors.

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[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Carbonium Ions. V. The Nature of the *t*-Butyl Cation as Indicated by a Study of the Formation of N-*t*-Butylacrylamide[1]

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The kinetics of the acid-catalyzed formation of N-*t*-butylacrylamide from *t*-butyl alcohol and acrylonitrile have been studied from 20–69% sulfuric acid. The rate is proportional to the first powers of the acrylonitrile concentration, the *t*-butyl alcohol concentration and the Hammett h_0 function. The rate constants for the reactions of protonated *t*-butyl alcohol with water, acrylonitrile and propionitrile were found to be identical within a factor of three. The combined results are interpreted in terms of transition states in which the incoming group is so weakly bonded to the transition state that its nature has only a small effect on the rate. The results do not support the concept of a free *t*-butyl cation. The rate of hydrolysis of acrylonitrile was studied from 28–85% sulfuric acid. The rate is proportional to the concentration of acrylonitrile and the h_0 function.

Since Whitmore[2] first introduced the concept of aliphatic cations, considerable controversy has existed as to their exact nature.

On the basis that methanolysis of hydrogen 2,4-dimethylhexyl-4-phthalate proceeded with 55% inversion and 45% racemization, Doering and Zeiss[3] concluded that no free alkyl cation was an intermediate. Their argument was that if the *t*-alkyl cation was not free enough to racemize, it is difficult to conceive of a transition state in which there is no covalent participation by the incoming group. Their conclusion is strongly supported by the failure to observe a mass-law effect in the solvolysis of *t*-alkyl halides.[4]

The strongest arguments proposed in favor of free *t*-alkyl cations are the studies of Winstein, Grunwald and Jones[5] on the variation of rate with solvent. We interpret these studies as showing that there is nearly complete charge separation in the transition state, a situation that can be accommodated by transition states of the type described by Doering and Zeiss.

In our work, a study of the acid-catalyzed reactions of *t*-butyl alcohol was initiated with the expectation that it would provide evidence as to the existence of the *t*-butyl cation as a reaction intermediate. It was first necessary to develop acidity function theory and this was the concern of an earlier paper.[6]

The reaction chosen for study was the formation of N-*t*-butylacrylamide from *t*-butyl alcohol and acrylonitrile. This reaction is of a type extensively studied by Ritter,[7] who demonstrated that it was a remarkably general reaction between alcohols and nitriles.

Experimental

Extinction Coefficients.—In order to determine the concentration of N-*t*-butylacrylamide spectroscopically, it was necessary to know the extinction coefficients for *t*-butyl alcohol and acrylonitrile (the reactants), N-*t*-butylacrylamide (the product), acrylamide (a side product) and acrylic acid (the hydrolysis product of acrylamide or N-*t*-butylacrylamide). The *t*-butyl alcohol and acrylonitrile showed no measurable absorption in the region of wave lengths greater than 220 mμ at the concentrations employed in the kinetic runs. Their absorptions were thus neglected. The absorption spectra of the remaining compounds are summarized in Table I.

Kinetic Measurements.—The kinetics of the reaction between *t*-butyl alcohol and acrylonitrile were studied in 20–69% sulfuric acid. The formation of the product, N-*t*-butylacrylamide, was determined spectroscopically with a Beckman DU spectrophotometer. Measurements were made at 260–280 mμ. The cells of the spectrophotometer were thermostated at 25 ± 0.1° by means of thermospacers. Rapid runs were conducted entirely in the spectrophotometer cells whereas slow runs were held in thermostated volumetric flasks from which a portion was periodically introduced into the cells.

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[1] Grateful acknowledgment is made of the support of this research by a grant from the Petroleum Research Fund of the American Chemical Society.

[2] F. C. Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

[3] W. E. Doering and H. Zeiss, THIS JOURNAL, **75**, 4733 (1953).

[4] L. Bateman, M. Church, E. Hughes, C. Ingold and N. Taher, *J. Chem. Soc.*, 979 (1940). Note comments of J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1956, pp. 103–105.

[5] E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948); S. Winstein, E. Grunwald and N. W. Jones, *ibid.*, **73**, 2700 (1951).

[6] N. Deno and C. Perizzolo, *ibid.*, **79**, 1345 (1957).

[7] J. Ritter and co-workers, *ibid.*, **70**, 4045, 4048 (1948); **71**, 4128, 4130 (1949); **73**, 4076 (1951); **74**, 763 (1952).