centrations of oxygen makes it evident that a hot radical mechanism will not suffice to explain this phenomenon. It is unlikely that oxygen would react so selectively with isopropyl rather than propyl radicals if these were formed in fixed proportion in the initial act or by immediately subsequent collisions.

**Proposed Role of HI.**—An alternative reaction path is outlined in the set of equations

$$CH_3CH_2CH_2I + h\nu \longrightarrow CH_3CH{=}CH_2 + HI \quad (9)$$

$$CH_3CH{=}CH_2 + I \rightleftarrows CH_3CHICH_2\cdot \quad (10)$$

$$CH_3CHICH_2\cdot + I_2 \rightleftarrows CH_3CHICH_2I + I \quad (11)$$

$$CH_3CH_2ICH_2\cdot + HI \longrightarrow CH_3CH_2ICH_3 + I \quad (12)$$

The sequence of reactions 10, 11 and 12 is quite plausible once the presence of hydrogen iodide is admitted, as it is known[15] that iodine strongly catalyzes the addition of hydrogen iodide to propylene even at −78°. Since propylene is found in the final products, this mechanism depends on hydrogen iodide as the essential intermediate in the formation of isopropyl iodide.

The effect of oxygen can be understood as the consumption of hydrogen iodide, most probably through the formation of peroxy-free radicals by either *n*-propyl or isopropyl radicals.

$$R\cdot + O_2 \longrightarrow RO_2\cdot \quad (13)$$

$$RO_2\cdot + HI \longrightarrow RO_2H + I \quad (14)$$

Hydrogen iodide, insofar as it is available, should react readily to form the hydroperoxide. In its absence the hydroperoxide would probably be formed by reaction with the substrate. This mechanism is also able to account for the observed increase in quantum yield in alkyl iodide photolyses conducted in air, since reaction 13 competes with reaction 5.

The hypothesis that hydrogen iodide is an intermediate in such a photolysis has been subjected to partial experimental test as follows: Air-free ethyl iodide was photolyzed at 30°, in the full light of the mercury lamp, in the presence of $I_2^{131}$ and an amount of propylene about three times as great as the amount of ethylene expected from the photolysis. The results are shown in Table V and they give some support to a mechanism involving hydrogen iodide production in the photolysis of an alkyl iodide.[16]

TABLE V

ACTIVITY IN CARRIER FRACTIONS AFTER PHOTOLYSIS OF ETHYL IODIDE CONTAINING PROPYLENE

| Propylene, moles/l. | EtI, % | *i*-PrI, % | *n*-PrI, % |
|---|---|---|---|
| $8.6 \times 10^{-3}$ | 81.9 | 16.1[a] | 1.0 |
| $1.5 \times 10^{-2}$ | 76.1 | 23.3 | 0.6 |

[a] An accident in this run made de-aeration less complete than usual, probably making this figure low.

Finally, it should be pointed out that the proposed reaction 9 is highly exothermic with light of 2537 Å. and the obvious proximity of the β-hydrogen to the iodine atom in the molecule may be significant. In fact, this may offer a possible explanation of the observed temperature coefficient of isomerization. Raman spectra of *n*-propyl iodide[17] show that both *trans* and *gauche* forms exist in the liquid state, while only one form exists in the solid state. In the *trans* form the two β-hydrogens are at equal distances from the iodine atom, while in the *gauche* form one is much closer than the other. A temperature coefficient on the *trans–gauche* ratio could account for the temperature coefficient of isomerization in the primary act.

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(15) M. S. Kharasch, J. A. Norton and F. R. Mayo, THIS JOURNAL, **62**, 81 (1940).

(16) More recent results of Mr. David Bunbury in this Laboratory clearly indicate the presence of HI in the products of photolysis of air-free ethyl iodide.

(17) S. Nakamura, *J. Chem. Soc. Japan*, **60**, 1010 (1939).

NOTRE DAME, INDIANA

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

# The Thermal Decomposition of Cyclopentanone[1,2]

BY EVERETT R. JOHNSON AND W. D. WALTERS

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The homogeneous thermal decomposition of cyclopentanone has been studied over the temperature range 488–543° at pressures from 99 to 314 mm. The principal reactions during the early stages of the decomposition yield the following products: (a) 2-cyclopenten-1-one and hydrogen, (b) butene-1 and carbon monoxide, and (c) ethylene and carbon monoxide. The pressure measurements and the analytical data indicate that the decomposition of cyclopentanone possesses an induction period and is not kinetically simple. The addition of butene-1 together with its decomposition products has been found to accelerate the decomposition of cyclopentanone at 512°.

Although no extensive study of the thermal decomposition of cyclopentanone appears to have been published in the literature, Ibuki[3] has reported that cyclopentanone decomposes in the region 530–550° to give chiefly lower unsaturated hydrocarbons and carbon monoxide with smaller amounts of saturated hydrocarbons and hydrogen. In addition, acetylene to the extent of 1 to 7% was found in the gaseous products. The photochemical decomposition of cyclopentanone which has been studied in several laboratories[4-6] involves a cleavage of the ring; the main gaseous

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(1) This work was supported by the Office of Naval Research.

(2) Abstracted from the Ph.D. thesis submitted by Everett R. Johnson.

(3) E. Ibuki, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **71**, 96 (1950).

(4) O. D. Saltmarsh and R. G. W. Norrish, *J. Chem. Soc.*, 455 (1935). In this study a mixture of butenes was reported in place of cyclobutane.

(5) S. W. Benson and G. B. Kistiakowsky, THIS JOURNAL, **64**, 80 (1942).

(6) F. E. Blacet and A. Miller, Abstracts, A. C. S. Meeting, Chicago, Illinois, September 6–11, 1953, p. 18R.

products appear to be carbon monoxide plus either ethylene or cyclobutane. Further study of the thermal decomposition of cyclopentanone seemed of interest for comparison not only with the thermal decompositions of related compounds but also with the photochemical results.

## Experimental

**Apparatus and Materials.**—Most of the experiments were conducted in a 370-ml. cylindrical Pyrex reaction vessel contained in an electrically heated furnace. The temperature was controlled by means of a thyratron circuit designed by Waring and Robison,[7] and the temperature at the center of the reaction bulb was measured with a platinum–platinum, 13% rhodium thermocouple connected to a Leeds and Northrup, Type K-2, potentiometer. The thermocouple was standardized at the melting points of aluminum and zinc. A second bulb packed with thin-walled Pyrex tubes provided a reaction vessel with a 22-fold increase in surface to volume ratio. The relatively high boiling point of cyclopentanone necessitated the heating of the external tubing, and to avoid heating the mercury manometer a click gage, which was calibrated before each experiment, was used.

The infrared absorption measurements were made with a Perkin–Elmer, Model 12B, instrument and the ultraviolet results were obtained with a Beckman, Model DU, spectrophotometer.

Cyclopentanone from either Eastman Kodak Company or Arapahoe Chemicals, Incorporated, was dried over anhydrous calcium sulfate and fractionated two or three times in an 85-cm. Lecky–Ewell column at a reflux ratio of about 6:1, the middle fraction in each distillation being used for the subsequent work. The distillations were carried out in the presence of an atmosphere of pure nitrogen and no peroxides could be detected in the purified material. The samples used for the kinetic studies ordinarily distilled over a one-tenth degree boiling range; the index of refraction of the purified material was found to be $n^{20}\text{D}$ 1.4370–1.4373 in agreement with values reported in the literature 1.4370[8] and 1.4371.[9]

Propylene (99.5%) was purchased from the Ohio Chemical and Manufacturing Company and butene-1 (99%) was supplied by the Matheson Company.

**Gaseous Products.**—The initial infrared examination of the gases produced at 508° indicated the presence of carbon monoxide, methane, ethylene and other unsaturated hydrocarbons. Then the usual methods of gas analysis were employed to determine the amounts of the various types of products formed in a series of experiments at 514° with initial pressures of 120–310 mm. and pressure increases from 15 to 60%. From three experiments carried to about 40% pressure increase the average composition of products volatile at $-78°$ was found to be: 0.4% absorbable in 40% potassium hydroxide, 16% higher unsaturates, 14% ethylene, 15% hydrogen, 37% carbon monoxide and 18% residue (saturated hydrocarbons). In this series the percentages of the unsaturates and hydrogen became smaller at the longer times of reaction.

In order to facilitate the infrared identification of the products as well as the analysis of the saturated hydrocarbons by the combustion procedure, the gaseous products were separated (before analysis) into several fractions by the utilization of differences in volatility. The reaction mixture upon removal from the heated vessel was passed through a series of four traps kept at $-10$, $-64$, $-78$ and $-196°$, respectively. With this arrangement most of the undecomposed cyclopentanone could be condensed in the first two traps without the removal of appreciable quantities of gaseous products. A more complete separation of the volatile reaction products was then made by the use of a Toepler pump and suitable cooling baths. Gas analyses were performed on the individual fractions. The results in terms of the over-all composition of the products will be given later in Table I. In two instances the saturated hydrocarbon residue in the $-196°$ fraction was not analyzed by combustion, but assumed to be methane; in another case the residue in the $-139°$ fraction was assumed to be ethane, and the $-110°$ residue, propane.

To secure larger quantities of the various fractions, the products were collected from several series of decompositions, each series consisting of about six 300 mm. experiments at 515–530° carried to about 30% pressure increase. Infrared measurements on the products resulted in the identification of propylene in the $-110°$ fraction and the observation that the infrared curve for the $-78°$ fraction is almost identical with that for butene-1. The infrared data also gave some evidence for the formation of small amounts of ethane and 1,3-butadiene, as well as a trace of acetylene, but no indication for the presence of cyclobutane in any fraction from $-110°$ to 0°. A small peak at 11.2 μ in the 0° fraction may indicate the presence of a small amount of cyclopentadiene.

Passage of the gaseous products through an alcoholic solution of silver nitrate and a solution of mercuric chloride gave positive tests for the presence of a trace of acetylene and negative tests for allene. In order to test for ketene separate experiments were performed at various temperatures from 453 to 526° (four in the unpacked bulb and two in the packed bulb). The products were taken out during the early stages of the decomposition and brought into contact with water which was later titrated with a sodium hydroxide solution. No experiment showed a definitely detectable amount of acetic acid, *i.e.*, greater than $2.5 \times 10^{-3}$ milliequivalent. Two experiments were performed to test for aldehydes in the products with Schiff's reagent and with Lewin's reagent[10]; in neither case could any aldehyde be found.

**Liquid Products.**—The liquid portion of the reaction mixture gave greater absorption than cyclopentanone (a) in the infrared region at about 13.3, 10.9, 10.0, 9.9, 9.2, 7.4, 7.0, 6.3 and 6.1 μ and (b) in the ultraviolet in the region from 240 to 224 mμ and presumably below. For the identification of the one or more compounds responsible for these absorptions, fractional distillations followed by chemical treatments and spectroscopic examinations were performed on the liquid products obtained in two ways: (1) from eighteen static experiments and (2) from flow experiments conducted at 720–900° under 10–20 mm. pressure in an apparatus similar to that used by Rice and his co-workers.[11]

The evidence which led to the conclusion that 2-cyclopenten-1-one is an important product may be summarized as follows. Infrared and ultraviolet examinations of the various fractions indicated that a product has a boiling point near that of cyclopentanone, probably slightly greater. The reported boiling point[12,13] of 2-cyclopenten-1-one is only five or six degrees higher than that of cyclopentanone. The intense ultraviolet absorption in the region 224–232 mμ pointed to the probable presence of an α,β-unsaturated ketone.[14,15] In two separate flow experiments the products which boiled at 128° and above were hydrogenated. The infrared and ultraviolet absorptions not belonging to cyclopentanone which could be observed before hydrogenation were essentially eliminated by the hydrogenation. Moreover, the reaction mixture before hydrogenation showed an absorption at about 5.86 μ noticeably greater than that observed for pure cyclopentanone; hydrogenation decreased the absorption at 5.86 μ and increased the absorption at 5.74 μ, as would be expected for the conversion of 2-cyclopenten-1-one into cyclopentanone.[16]

The liquid products were also treated by a procedure which was a modification of one used previously for the transformation of substituted 2-cyclopenten-1-ones into substituted succinic acids.[15] Ozone was bubbled through a glacial acetic acid solution of the liquid products for several hours followed by the addition of 12% hydrogen peroxide,

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[7] C. E. Waring and G. Robison, *Rev. Sci. Instruments*, **14**, 143 (1943).

[8] C. R. Noller and R. Adams, THIS JOURNAL, **48**, 1080 (1926).

[9] The value $n^{15}\text{D}$ 1.43917 given by J. Timmermans and Mme. Hennaut-Roland, *J. chim. phys.*, **34**, 693 (1937), has been corrected to 20°.

[10] L. Lewin, *Ber.*, **32**, 3388 (1899).

[11] F. O. Rice, P. M. Ruoff and E. L. Rodowskas, THIS JOURNAL, **60**, 955 (1938).

[12] M. Godchot and F. Taboury, *Bull. soc. chim., France*, [4] **13**, 545 (1913).

[13] B. K. Merejkowsky, *ibid.*, [4] **37**, 1174 (1925).

[14] A. E. Gillam and T. F. West, *J. Chem. Soc.*, 486 (1942).

[15] R. L. Frank, R. Armstrong, J. Kwiatek and H. A. Price, THIS JOURNAL, **70**, 1379 (1948).

[16] R. N. Jones, V. Z. Williams, M. J. Whalen and K. Dobriner, *ibid.*, **70**, 2024 (1948); H. L. Cupples, *ibid.*, **72**, 4522 (1950).

steam distillation and evaporation. The solid which separated had a melting point of 183° without recrystallization and formed a *p*-toluidide melting at 264–266°. The *p*-toluidide from known succinic acid melted at 262–265°[17] and the mixed melting point was 262–264°. Pure cyclopentanone when treated similarly did not yield any succinic acid.

The fractions from the combined static experiments boiling in the range 120–128° appeared to have an absorption in the region 13.5–13.8 μ greater than could be attributed to 2-cyclopenten-1-one. However, various substances reported as products from reaction mixtures containing butenes and butadiene[18,19] have an infrared absorption in this region.

**2-Cyclopenten-1-one.**—That this compound is present in the liquid portion of the reaction mixture was verified by the fact that the samples of 2-cyclopenten-1-one prepared in two different ways[12,20] showed infrared absorptions at the points listed above for the liquid product. As others have observed, the preparation of this unsaturated ketone is not free from difficulty and in neither case was an analytically pure sample obtained. However, the 2,4-dinitrophenylhydrazine derivative had a melting point of 165° in agreement with Dane and Eder's value.[20] The ultraviolet absorption spectrum of the prepared 2-cyclopenten-1-one exhibited a sharp rise in the region 240–220 mμ.[21]

Several preliminary decomposition experiments were performed with 2-cyclopenten-1-one because of its presence during the cyclopentanone decomposition. A decomposition occurs at 512°, but with a slightly impure sample the measured rates are probably not of significance. The fraction volatile at −196° contained 72% carbon monoxide and 11% hydrogen indicating that the ring cleavage is considerably more important than any dehydrogenation. An infrared examination indicated that in the second fraction volatile at −95° ethylene is an important constituent and that not more than a small amount of acetylene is present. The infrared curve for the third fraction, volatile at −40°, agreed very closely with that of pure 1,3-butadiene. No positive evidence for the presence of cyclopentadienone was obtained. The products show that a major reaction in the decomposition is

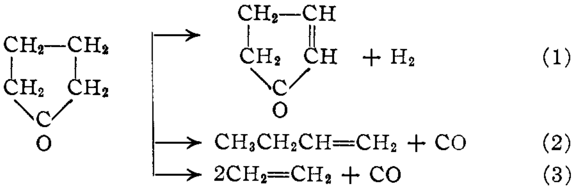
$$C_5H_6O \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + CO$$

This same reaction has been suggested to account for the low yield of 2-cyclopenten-1-one and the presence of carbon monoxide and butadiene in the distillation of the calcium salt of hydromuconic acid.[13]

Since the ultraviolet absorption of the cyclopentanone products at 224 mμ which is shown later in Fig. 1 is probably caused chiefly by 2-cyclopenten-1-one, the change in the pressure of this intermediate could be calculated from the absorption data plus a knowledge of the molar extinction coefficient. From the absorption curve measured for the not completely pure sample prepared above and the literature values[21,22] reported for wave lengths other than 224 mμ the value of the molar extinction coefficient in 95% ethanol appears to be about 8 × 10³ at 224 mμ.

## Results

**Products of the Reaction.**—In addition to the analytical results given above, detailed gas analyses were obtained for the reaction mixture at increasing percentages of decomposition. The results are summarized in Table I. On the basis of the various analytical data the most important over-all reactions appear to be



$$\longrightarrow CH_3CH_2CH{=}CH_2 + CO \quad (2)$$

$$\longrightarrow 2CH_2{=}CH_2 + CO \quad (3)$$

The analyses indicate that secondary reactions cause the consumption of hydrogen and unsaturated hydrocarbons with a simultaneous increase in the lower saturated hydrocarbons, particularly methane. Butadiene is probably a secondary product resulting partly from the dehydrogenation of butene-1 and partly from the decomposition of 2-cyclopenten-1-one. Propylene is known to arise from the pyrolysis of butene-1[18,23] so that it is not necessarily produced from cyclopentanone directly. It is apparent that reactions other than (1) to (3) occur either subsequently or simultaneously since the amounts of the unsaturated hydrocarbons are not equivalent to those of carbon monoxide.

A comparison with the photochemical studies[4–6] shows that reaction (3) appears in both types of decomposition, but the two other reactions do not appear to occur in the photolysis. Instead a reaction to form cyclobutane is an important process in photochemical decomposition. One would probably not expect to find cyclobutane in the thermal decomposition since it undergoes a rapid decomposition at somewhat lower temperatures.[24]

TABLE I

PERCENTAGE COMPOSITION OF THE GASEOUS PRODUCTS FROM THE DECOMPOSITION OF CYCLOPENTANONE AT 515°[a,b]

| $\Delta P/P_0$, % | $H_2$ | CO | $C_2H_4$ | $C_3H_6$[d] $C_4H_8$ | $CH_4$ | $C_2H_6$ | $C_3H_8$ |
|---|---|---|---|---|---|---|---|
| 15 | 22 | 41 | 13 | 15 | 5 | 3 | 2 |
| 28 | 14 | 37 | 17 | 20 | 7 | 5 | 0.5 |
| 52 | 14 | 41 | 14 | 14 | 11 | 6 | [c] |
| 54 | 10[e] | 42[e] | 13[e] | 15[e] | 12[e] | 6[e] | 1[e] |
| 79 | 12 | 40 | 12 | 10 | 12 | 8 | 2 |
| 121 | 11 | 42 | 7 | 8 | 18 | 10 | 2 |

[a] The third and fourth experiments are at 513°. [b] The initial pressures of the experiments in order listed are: 200, 246, 161, 268, 268 and 279 mm. The reaction times are: 21, 31, 54, 54, 70 and 158 min. [c] In a similar experiment 1% $C_3H_8$ was found by combustion analysis. [d] With the exception of the fourth experiment this column represents gases absorbable in 87% sulfuric acid and will include butadiene plus other unsaturates volatile at −50°. [e] Mass spectrometric analyses. The results show 10.2% butenes, 5.1% propylene, 1.2% butadiene, 0.2% cyclopentadiene, 0.5% other unsaturates and 0.2% *n*-butane.

**Homogeneity.**—Experiments were performed with the unpacked and packed reaction vessels for initial pressures of 125–150 mm. at 519 and 530°. The rates in the packed vessel, as measured by the percentage pressure increase after 22–25 minutes, did not average more than 15% greater than the rates in the unpacked vessel under similar conditions. Since the packed vessel provided a

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(17) The value reported by C. R. Barnicoat, *J. Chem. Soc.*, 2926 (1927) is 260° (uncor.).

(18) R. V. Wheeler and W. L. Wood, *ibid.*, 1819 (1930).

(19) G. B. Kistiakowsky and W. W. Ransom, *J. Chem. Phys.*, **7**, 725 (1939).

(20) E. Dane and K. Eder, *Ann.*, **539**, 207 (1939); S. David, G. DuPont and C. Paquot, *Bull. soc. chim., France*, [5] **11**, 561 (1944).

(21) Since the completion of this work, H. Adkins and S. H. Watkins, THIS JOURNAL, **73**, 2184 (1951), have reported a maximum at 218 mμ and a 2,4-dinitrophenylhydrazone melting at 169–169.5°.

(22) H. S. French, THIS JOURNAL **74**, 514 (1952)

(23) C. D. Hurd and A. R. Goldsby, *ibid.*, **56**, 1812 (1934).

(24) C. T. Genaux and W. D. Walters, *ibid.*, **73**, 4497 (1951).

22-fold increase in surface to volume ratio, it appears that the amount of decomposition occurring on the surface of the unpacked vessel is not more than 1 or 2% of the total reaction.

**Rate Experiments.**—Curve 1 in Fig. 1 shows a typical pressure–time curve for the decomposition of 140 mm. of cyclopentanone at 512°. The shape of this curve with its apparent induction period indicates that the rate of pressure increase during the thermal decomposition of cyclopentanone does not obey a simple first- or second-order rate law. Experiments in which the click gage was replaced with a heated mercury manometer also showed that the initial rate of pressure increase is not the maximum rate.[25] It was observed that in two experiments cyclopentanone containing 10–13% of added 2-cyclopenten-1-one still gives a pressure–time curve showing a rate which increases during the early stages of the reaction. This indicates that the s-shaped nature of the curve is not entirely the result of the building up of small amounts of 2-cyclopenten-1-one as an intermediate.

The changes in the amounts of several of the components of the reaction mixture with time are also given in Fig. 1. Curve 2 represents the percentage of the carbonyl group that has disappeared after definite times of reaction. The amount of carbonyl disappearing was determined from the difference between the initial quantity of cyclopentanone and the quantity of carbonyl measured by the hydroxylamine analysis[26] of the reaction mixture. The latter includes both cyclopentanone and the intermediate 2-cyclopenten-1-one. If 2-cyclopenten-1-one is the only carbonyl compound present in addition to cyclopentanone, curve 2 will give the over-all rate of ring cleavage. For comparison the amounts of carbon monoxide with increasing time are shown on the same plot. The close agreement between the carbon monoxide formed and the carbonyl disappearing during the initial portion of the decomposition gives evidence that other oxygen-containing compounds do not appear as products in significant amounts. In this connection it should be noted that a test with anhydrous copper sulfate did not show the presence of water in the products which might have resulted from a dehydration reaction and which has been observed under certain conditions for cyclic ketones.[21,27]

The quantity of hydrogen present during the reaction is given by curve 3. If hydrogen is not disappearing rapidly by secondary reactions in the early stages of the decomposition, this curve provides an indication of the magnitude of the dehydrogenation reaction. The points at 66 min. for hydrogen and carbon monoxide which do not lie on the curves are no doubt in error since similar plots at 515° carried to 170 min. do not show a decrease at the corresponding time. The change in the ultraviolet absorption of a solution of the products at 224 mμ as the decomposition progresses is shown by curve 4. If this absorption is due mainly to the concentration of 2-cyclopenten-1-one, the fact that a maximum is reached and followed by a slow decrease is indicative of the subsequent decomposition of this compound.[28]

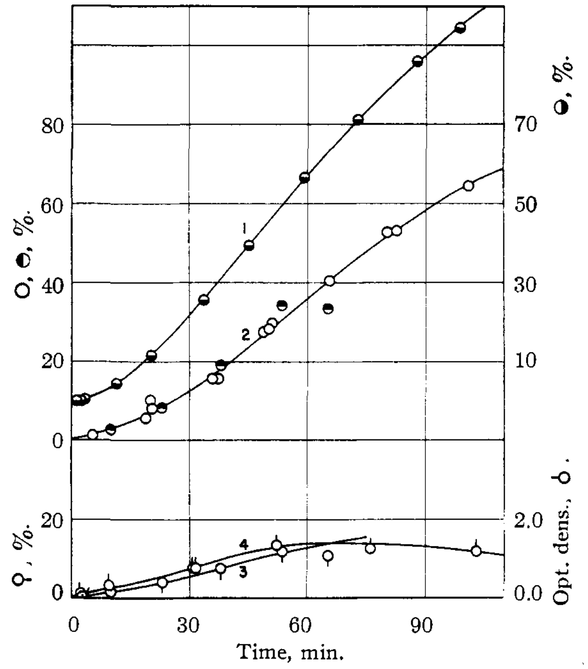

Fig. 1.—Decomposition of cyclopentanone at 512.5° ± 1°: ◒, represents the % pressure increase, $P_0$ = 140 mm.; ○, the percentage of carbonyl which has disappeared, $P_0$ = ~143 mm.; ◐, amount of carbon monoxide formed (as percentage of initial pressure), $P_0$ = ~158 mm.; ⫯, amount of hydrogen formed (as percentage of the initial pressure), $P_0$ = ~158 mm.; ⫰, absorption at 224 mμ of the reaction products from 153 mm. of cyclopentanone if dissolved in 0.9 l. solvent of (1 cm. light path).[28]

By the use of the results for the disappearance of carbonyl (curve 2) with the data for the amount of dehydrogenation to 2-cyclopenten-1-one (based on either the hydrogen analyses or the observed ultraviolet absorption), the amounts of cyclopentanone which have disappeared after definite times can be calculated and plotted. Such a plot shows that the rate of disappearance of cyclopentanone also is not a maximum at the start of the reaction. Likewise the curve for the ethylene present during the decomposition shows an induction period.

The results from a series of experiments carried out at 512° with different initial pressures are shown in Fig. 2. Both the percentage of carbonyl disappearing and the percentage pressure rise during 51 minutes undergo an increase as the initial pressure is increased. Since the maximum slope of the pressure–time curve is usually reached by the time the pressure has risen 30%, the rates of pressure rise were determined (after 30% pressure increase) for the experiments at the different initial

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[25] Unpublished results of W. T. Barry, Jr., obtained in this Laboratory.

[26] W. M. D. Bryant and D. M. Smith, THIS JOURNAL, **57**, 57 (1935).

[27] C. D. Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Company, New York, N. Y., 1929, p. 258.

[28] Multiplication of the optical density values by a factor of ten will give approximately the percentage of cyclopentanone converted into 2-cyclopenten-1-one. This factor is based on two assumptions: (a) no other product contributes significantly to the absorption and (b) the molar extinction coefficient for 2-cyclopenten-1-one is about 8 × $10^3$ at 224 mμ.

pressures. By means of a log-log plot it was found that $(dP/dt)_{30\%}$ is approximately proportional to the 1.2 power of the initial pressure. In the decompositions of cyclopentane and tetrahydrofuran which also have s-shaped pressure–time curves the maximum rate of pressure increase has been found to be proportional to the 1.5 power of the initial pressure.[29]

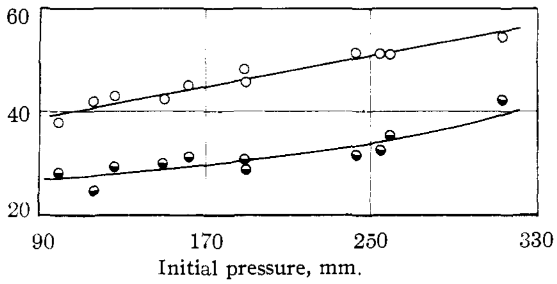

Fig. 2.—Effect of initial pressure upon the decomposition of cyclopentanone at 512.5°, reaction time, 51.4 mm.: ○, % pressure increase; ◒, percentage of carbonyl disappearing.

Other experiments which are summarized in Table II were conducted at temperatures from 488 to 543° for times of reaction chosen to give approximately the same amount of decomposition. In view of the complexity of cyclopentanone decomposition the variation of the rate of carbonyl disappearing or of pressure rise will probably not correspond to any single process. Nevertheless it was of interest to calculate values of the "apparent activation energy" from (a) the percentage of carbonyl disappearing considered both as a first order and as a three-halves order process and (b) from rate constants calculated by dividing $(dP/dt)_{30}$ by $P_0^{1.2}$. These calculations indicated that the "apparent activation energy" is within the range 62 ± 2 kcal. per mole.

TABLE II

THE RATE OF DISAPPEARANCE OF CARBONYL AT DIFFERENT TEMPERATURES

| Temp., °C. | Time, min. | $P_0$, mm. | Carbonyl disappearing, % |
|---|---|---|---|
| 488 | 200.9 | 147 | 31.6 |
| 491 | 178.4 | 126 | 29.2 |
| 500 | 115.4 | 130 | 32.0 |
| 511 | 61.7 | 156 | 30.8 |
| 523 | 30.7 | 161 | 32.7 |
| 530 | 25.0 | 174 | 32.0 |
| 543 | 12.9 | 162 | 32.5 |

**Effect of Added Substances.**—In view of the shape of the curves shown in Fig. 1 and the fact that unsaturated hydrocarbons accelerate the decompositions of certain other cyclic compounds,[29] butene-1 and propylene, which are present in the reaction products, were tested for an accelerating effect upon the decomposition of cyclopentanone. The results of experiments in which carbonyl analyses were made are shown in Table III. In the presence of considerable quantities of propylene there is some acceleration, but the effect which results from the addition of butene-1 plus its decomposition products is quite marked. It is apparent that the inert gas nitrogen does not have a similar influence.

TABLE III

EFFECT OF PROPYLENE AND BUTENE-1 UPON THE CYCLOPENTANONE DECOMPOSITION

Temp., 512°; reaction time, 51.4 min.

| $P°_{C_5H_8O}$, mm. | Added subst. | $P_{A.S.}$, mm. | Carbonyl disappearing, % |
|---|---|---|---|
| 162 | ........ | 0 | 31 |
| 165 | Propylene[a] | 147 | 41 |
| 156 | Propylene[a] | 164 | 41[c] |
| 148 | Butene-1[a] | 168 | 61 |
| 139 | Butene-1[b] | 148 | 65 |
| 146 | Nitrogen | 132 | 31 |
| 150 | ........ | 0 | 30 |

[a] Substance in the reaction vessel for 5–10 min. before the introduction of cyclopentanone. [b] Butene-1 remained in the reaction vessel 35 min. and underwent a 28% pressure increase before the introduction of cyclopentanone. [c] Temperature, 513° in this experiment.

The effect of butene-1 upon the dehydrogenation reaction was investigated by allowing about 150 mm. of cyclopentanone to react at 512° with and without the simultaneous introduction of 55 mm. of butene-1. To avoid interference by any butadiene only the products condensable at −60° under vacuum and non-volatile at −60° after 30 minutes pumping were subjected to ultraviolet absorption analysis. By this procedure it was found that the 2-cyclopenten-1-one in the products after 11 min. in the presence of butene-1 is slightly more than that present in the normal decomposition after 32 min.

Since nitric oxide is able to inhibit certain free radical chain processes, two experiments were performed in which nitric oxide (~1 and 8 mm.) was added to 160–170 mm. of cyclopentanone at 513°. The pressure increase observed after 20 min. indicated an acceleration rather than an inhibition by the added nitric oxide.

**Discussion.**—The experimental results indicate that the decomposition of cyclopentanone does not proceed as a kinetically simple process. In many respects the decomposition is similar to that observed for cyclopentane. Both compounds yield products formed by dehydrogenation and by ring cleavage. With neither compound is the rate of the over-all reaction as large at the start as at a later time. With cyclopentanone, as in the case of cyclopentane, unsaturated compounds can accelerate the decomposition. In fact, some of the increase in the rate of the cyclopentanone decomposition as the reaction proceeds can be attributed to the accelerating influence of the unsaturated hydrocarbons or their decomposition products which are formed during the reaction. Whether the acceleration is a molecular reaction or a radical process has not been established.

With respect to the ring cleavage no definite evidence for the presence of biradicals has been obtained, but there is the possibility of the intermediate formation of tetramethylene acyl or the

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(29) L. Küchler, *Z. physik. Chem.*, **B53**, 307 (1943); D. W. Vanas, N. M. Lodge and W. D. Walters, THIS JOURNAL, **74**, 451 (1952); C. H. Klute and W. D. Walters, *ibid.*, **68**, 506 (1946); G. McDonald, N. M. Lodge and W. D. Walters, *ibid.*, **73**, 1757 (1951).

tetramethylene biradicals which have been assumed to be intermediates in the photolysis of cyclopentanone.[5,6] The formation of butene and ethylene from the tetramethylene biradical has been observed by Bawn and Milsted[30] in their study of the reaction of 1,4-dibromobutane and sodium at 300°.

In spite of the data which are available the complexity of the cyclopentanone decomposition precludes a thorough consideration of the detailed mechanism at the present time.

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ROCHESTER, N. Y.

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[30] C. E. H. Bawn and J. Milsted, *Trans. Faraday Soc.*, **35**, 889 (1939).

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

# The Thermal Decomposition of Cyclobutanone[1]

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The homogeneous thermal decomposition of cyclobutanone has been investigated over the temperature range 333–373°. The decomposition proceeds essentially by a reaction forming ethylene and ketene as the primary molecular products. For experiments conducted at initial pressures from 10 to 88 mm. at 368° first-order kinetics were observed. The change in rate constant with temperature is given by the relationship $k = 3.6 \times 10^{14} e^{-52000/RT}$ sec.$^{-1}$. The decomposition is not inhibited by the addition of propylene, toluene or nitric oxide.

In view of the apparent simplicity of the homogeneous thermal decomposition of cyclobutane[2] which forms two molecules of ethylene by a nonchain process, it was of interest to investigate the products and kinetics of the thermal decomposition of cyclobutanone as another example of a compound having a four-membered ring structure. The photochemical decomposition of cyclobutanone has been investigated already.[3,4] Benson and Kistiakowsky[3] found that ethylene and ketene, as well as propylene and carbon monoxide, are formed by the ultraviolet irradiation of cyclobutanone, indicating that at least two reaction paths are possible photochemically. The analytical results did not permit a decision concerning the presence or absence of cyclopropane. Recently Blacet and Miller[4] have observed that cyclopropane predominates over propylene in the photolysis at 3130 Å. but is approximately equal to propylene at 2654 Å.

## Experimental

**Materials and Apparatus.**—Cyclobutanone from two different sources was used in the present work. Sample A which was a purified sample prepared by the method of Roberts and Sauer[5] was generously furnished by Dr. F. E. Blacet. Measurement of the index of refraction gave values in the range 1.4198–1.4182 for temperatures 25.1–26.0° in comparison with a reported value[5] of $n^{25}\text{D}$ 1.4189. This sample was used without further treatment except that drying over anhydrous calcium sulfate or separation into several fractions by trap to trap distillation under vacuum was performed on the material before certain experiments. Sample B which was supplied by the Chemicals Procurement Company was purified by preparation of the semicarbazone; the regenerated ketone was fractionated in a spinning band column. The various fractions of the samples are designated by I, II, etc. Infrared absorption curves were obtained for samples AI, BII, BIII and BIV; they agreed well with each other and with a published curve[5] except for the possible presence of a trace of water in BII. In some of the experiments BII was dried before use, but no significant difference in rate was observed. In order to carry out a different type of purification several fractions from each of the samples above were combined and converted into the bisulfite derivative. The material regenerated from the bisulfite derivative will be referred to as sample C. Vapor pressures[6] of several portions were measured and compared with the values calculated from Benson and Kistiakowsky's equation.[3]

Propylene (99.5%) was obtained from the Ohio Chemical and Manufacturing Company and was subjected to repeated degassing at −196°. Nitric oxide (98%) supplied by the Matheson Company was purified by two distillations from −160 to −196°. Analyzed reagent grade toluene was dried over anhydrous calcium sulfate. All materials were thoroughly degassed just before introduction into the reaction vessel.

The early experiments were performed in a 360-ml. Pyrex reaction bulb with a thermocouple well at its center. Temperatures were measured with a platinum, platinum–13% rhodium thermocouple attached to a Leeds and Northrup Type K-2 potentiometer. The mercury manometer (3 mm. bore) was heated electrically to prevent the condensation of cyclobutanone. In some experiments a reaction vessel packed with thin-walled Pyrex tubes was used; this bulb provided a 17-fold increase in the surface to volume ratio. Most of the experiments were carried out in a second apparatus with an unpacked cylindrical Pyrex vessel of 500-ml. capacity. The furnace and apparatus for temperature control were a modification of a type previously used.[7] The temperature was measured with another platinum, platinum–13% rhodium thermocouple connected either to the Type K-2 potentiometer or to a Gray Model E-3040 potentiometer. The thermocouple was standardized at the melting point of zinc. Pressures below 17 mm. were measured with a 20 mm. bore mercury manometer read with a cathetometer. Pressures above 17 mm. were measured with a 6 mm. bore mercury manometer which was heated when necessary to avoid condensation.

In a series of experiments at 368° the rate of decomposition in the packed bulb with a 17-fold greater surface to volume

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[1] This work has been supported by a grant from the Celanese Corporation of America.

[2] C. T. Genaux and W. D. Walters, THIS JOURNAL, **73**, 4497 (1951); C. T. Genaux, F. Kern and W. D. Walters, *ibid.*, **75**, 6196 (1953).

[3] S. W. Benson and G. B. Kistiakowsky, *ibid.*, **64**, 80 (1942).

[4] F. E. Blacet and A. Miller, Abstracts, A. C. S. Meeting, Chicago, Illinois, September 6–11, 1953, p. 18R.

[5] J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949).

[6] The following list gives the sample designation followed by the temperature, the observed vapor pressure in mm., and the calculated value in parentheses. A: 0°, 10.9 (10.3); 23.2°, 38.8 (38.7). BII: 0.2°, 11.0 (10.5); 22.8°, 40.2 (37.9). BIII: 0.2°, 10.4 (10.5); 22.9°, 37.1 (38.1); 23.8°, 39.7 (40.0). C: 0.2°, 11.2 (10.5).

[7] D. W. Vanas and W. D. Walters, THIS JOURNAL, **70**, 4035 (1948).