is further indication that the time of mixing was poorly defined.

Summary

The velocity of saponification of acetylsalicylic acid at 35° has been investigated by the calorimetric method. The results agree well with the requirements of Brönsted's theory. The heat data obtained in these experiments are unsatisfactory.

Measurements of the heat of ionization of acetylsalicylic acid at 35° lead to the value $\Delta H_A = -3500$ joules per mole.

NEW HAVEN, CONNECTICUT RECEIVED OCTOBER 16, 1941

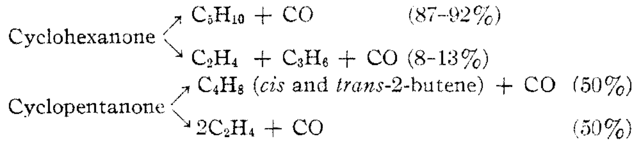
[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

The Photochemical Decomposition of Cyclic Ketones

BY S. W. BENSON AND G. B. KISTIAKOWSKY

The work of Norrish, *et al.*,[1,2] on the photochemical decomposition of cyclic ketones has indicated the formation of free bi-radicals in the primary process. The results, however, were complicated and there are some objections to the experimental techniques employed. Furthermore, the reported identification of gaseous products can be questioned because of the use of incorrect physical constants from the literature. On these grounds it seemed desirable to repeat the work on cyclopentanone and cyclohexanone, and then to extend it to cyclobutanone, using modified techniques.

The results of this investigation are in general agreement with the results of Norrish, the main discrepancies existing in the identification of the gaseous hydrocarbons. Norrish's results can be summarized thus



$$\text{1. Cyclohexanone} \begin{cases} \nearrow C_5H_{10} + CO & (87\text{-}92\%) \\ \searrow C_2H_4 + C_3H_6 + CO & (8\text{-}13\%) \end{cases}$$

$$\text{2. Cyclopentanone} \begin{cases} \nearrow C_4H_8\ (\textit{cis}\text{ and }\textit{trans}\text{-2-butene}) + CO & (50\%) \\ \searrow 2C_2H_4 + CO & (50\%) \end{cases}$$

In his first paper Norrish identified the C_5H_{10} as cyclopentane, but in his second paper he found a compound which boiled at 39° which was taken to be 1-pentene. However, the rather accurate work of Sherrill[3] gives the boiling point of 1-pentene as 29.0° and the boiling point of 2-pentene as 36°, this latter being in fact the highest boiling C_5H_{10} olefin. This would make it seem more likely that Norrish obtained a mixture of cyclopentane (b. p. 49°) and of one or more of the pentenes. In the present work the C_5H_{10} hydrocarbon was identified as a mixture of 75% cyclopentane and 25% 1-pentene. Except possibly for the proportions, this is probably the same mixture as obtained by Norrish.

Norrish identified the C_4H_8 hydrocarbon obtained from the cyclopentanone as a mixture of *cis*- and *trans*-2-butenes, but the vapor pressure measurements he gives show the vapor pressure to be below the vapor pressure of the highest boiling butene,[4] and the melting point of −96° is higher than that of the highest melting butene, *cis*-2-butene (m. p. −107°). In the present work the C_4H_8 hydrocarbon was positively identified as cyclobutane.

The experimental objection to the work of Norrish is that he refluxed the ketone past the source of light, and allowed the condensed vapors to flow back through the irradiated zone. This means that a considerable fraction of the light may have been absorbed by the *liquid*, and hence some of the reaction may have occurred in the liquid phase. This may contribute to the difference in the two sets of experimental results reported by Norrish, although he himself gives a different and plausible explanation of the discrepancy.

The decomposition of the cyclic ketones is important in that it provides a convenient method for studying the behavior of divalent free radicals and the mechanism of ring closure in the gaseous phase. The present work has been primarily concerned with the qualitative study of the products of photolysis, but future quantitative measurements will certainly provide interesting information on the above problems. An incidental consequence of the present work is that a convenient method of preparation of cyclobutane has

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(1) Saltmarsh and Norrish, *J. Chem. Soc.*, 455 (1935).

(2) Bamford and Norrish, *ibid.*, 1421 (1938).

(3) Sherrill, *J. Chem. Phys.*, **4**, 751 (1936).

(4) Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 876 (1935).

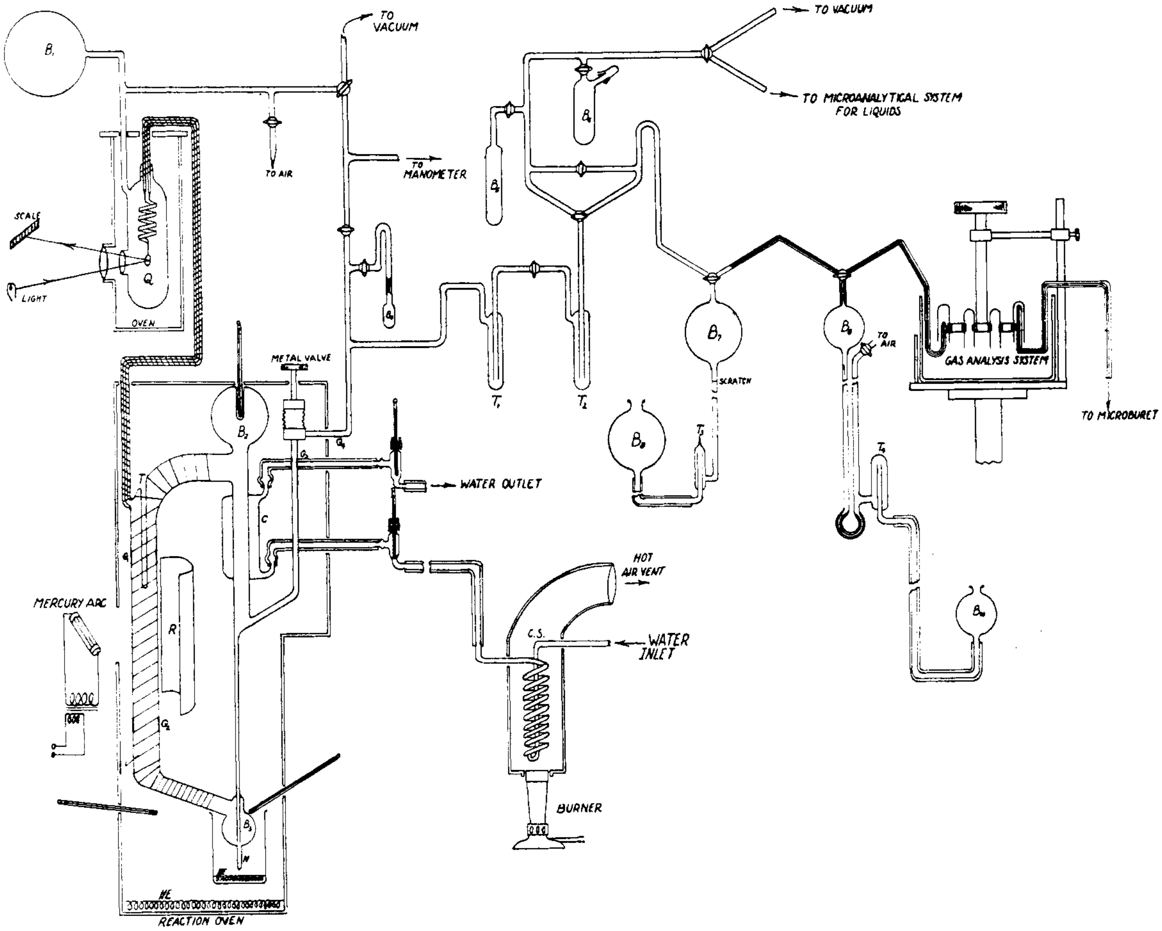

Fig. 1.—The reaction system: B_1, 1-liter ballast flask; B_2, 300-cc. ballast flask; B_3, 25-cc. boiler; B_4, storage bulb for collecting ketonic residues; B_5, shielded storage bulb for pure ketones; B_6, bulb with ground glass joint for introducing ketones in system; B_7, Toepler pump for separation of fractions; B_8, Toepler pump and manometer for storage, measurement and transfer of fractions; B_9, B_{10}, levelling bulbs for Toepler pumps; C, condenser; C. S., copper spiral for preheating water for condenser; G_1, G_2, quartz to Pyrex, graded seals; G_3, G_4, Kovar to Pyrex, graded seals; HE, nichrome spiral heating elements; N, nipple for collecting polymer; Q, quartz spiral manometer; R, stainless steel, cylindrical reflector; T, thermocouple well; T_1, T_2, traps for fractionation of products; T_3, T_4, traps to collect air from mercury levelling bulbs.

been found, a hydrocarbon whose use has been very restricted heretofore because of the difficulty of its preparation.

Experimental

Flow System.—The flow system is shown in Fig. 1. About 5 g. of ketone was distilled under vacuum from a reservoir into Trap (T_1) and then into the Bulb (B_3). The system was then closed by means of the metal valve and heated to the proper temperature. The rate of boiling of the ketone was controlled by an electrically operated heating element surrounding Bulb (B_3), and its vapor pressure was controlled by keeping the Condenser (C) at constant temperature with preheated water. The ketone vapor was preheated by a nichrome heating coil wrapped on the tube, and its temperature measured by a chromel-alumel thermocouple in a well lying a bit above the illuminated zone. Its pressure was measured by a quartz spiral manometer. In the period of a run the temperature was constant to within ±5°, and the pressure constant to within ± 10 mm. With the exception of the quartz chamber which was exposed to radiation, the entire apparatus was shielded from stray radiation by wrapping it in asbestos and aluminum foil. The quartz tube was 0.75 inch in diameter, and was sealed to the system by quartz-to-Pyrex graded seals. A nipple (N) was provided at the bottom of the pot in which polymeric materials could be collected at the end of each run after fractionating off the ketone. This was necessary only in the case of cyclohexanone since there was no polymer formation in the other decompositions. Blank runs were made with each ketone to establish the fact that no reaction took place in the absence of light.

The original technique employed was to follow the change in pressure during the course of the reaction, but since this did not allow very good control of the conditions, another technique was adopted which consisted of continuously pumping off the reaction products while keeping the temperature and pressure reasonably constant. This was done by bleeding the system through the metal valve. With cyclohexanone and cyclopentanone the two techniques gave identical results. Only the latter technique was employed with cyclobutanone.

By the use of microtechniques for the identification of the products and of a powerful source of ultraviolet radiation, it was possible to cut down the length of runs to thirty minutes. This is to be contrasted with the four to twenty hours taken by Norrish for his runs.

The source of illumination was a 1-kw., high-pressure, water-cooled mercury arc manufactured by the General Electric Company. It is described in one of their bulletins[5] (Type H-6) and gives an almost continuous source of radiation in the ultraviolet with reversal of the resonance lines. It is admirable for this type of work but cannot be used for quantitative measurements because of the rapid decay of the UV radiation intensity.

Purification of Materials.—Cyclohexanone was purified by crystallization of a middle fraction of the Eastman Kodak Co. product. It was crystallized as the semicarbazone and recrystallized to constant melting point, 164.9–165.9°. The semicarbazone was then dissolved in 10% sulfuric acid and the free ketone steam distilled. This was dried over anhydrous potassium carbonate and fractionated in a 3-ft. vacuum-jacketed still of 5-mm. bore packed with glass helices. The final sample was the middle fraction, b. p. 155.0° (765 mm.), $n^{20}\text{D}$ 1.4500. It was put through two bulb-to-bulb isothermal distillations under vacuum, and stored in a reservoir bulb wrapped in black paper and tin foil to protect it from light.

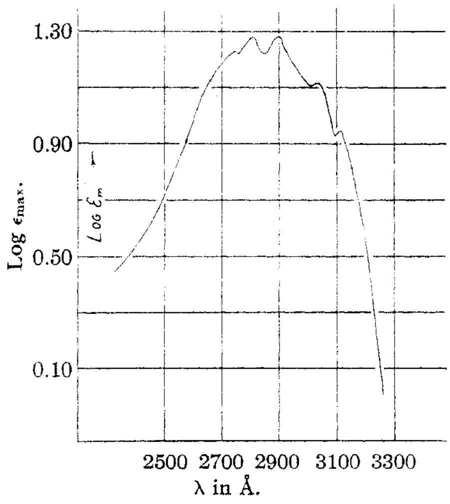

Fig. 2.—The absorption spectrum of cyclobutanone in hexane: $E_m = (1/cL) \log (I_0/I)$; c is concentration of the solute in moles/liter; L is length of the absorption cell = 1 cm.

Cyclopentanone was purified by successive fractionation of the Eastman product in the still described. The final sample had a b. p. 130.6–130.9° (771 mm.) and $n^{20}\text{D}$ 1.4332. It was given the same treatment as the hexanone before storing.

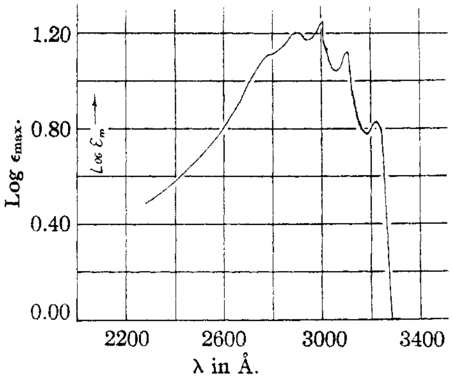

Fig. 3.—The absorption spectrum of cyclopentanone in hexane: $E_m = (1/cL) \log (I_0/I)$; c is concn. of solute in moles/liter; L is length of absorption cell = 1 cm.

Cyclobutanone was prepared for us by Mr. F. E. Condon in the Converse Laboratory, by the reaction of ketene and diazomethane. It was recrystallized as the semicarbazone, m. p. 204–205°, and recovered by steam distillation from sulfuric acid. The ketone was then dried over anhydrous calcium chloride and fractionated in the above-mentioned still. The final fraction had a b. p. 98.4–99.3° (762 mm.) and $n^{20}\text{D}$ 1.4215. It was given the same treatment as the other ketones and stored under vacuum.

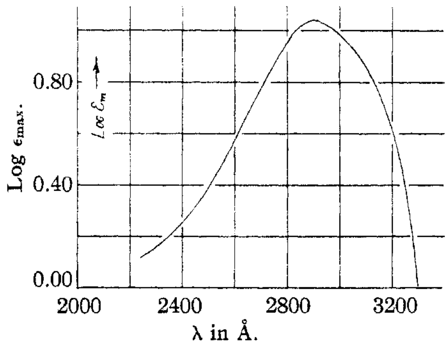

Fig. 4.—The absorption spectrum of cyclohexanone in hexane: $E_m = (1/cL) \log (I_0/I)$; c is concn. of solute in moles/liter; L is length of absorption cell = 1 cm.

Absorption Spectra.—Samples of the purified ketone were given to Mr. J. J. Leavitt who made quantitative measurements of their absorption spectra in *n*-hexane solution. The apparatus and method have been de-

TABLE I

Compound	Log E_{max}	Å.
Cyclobutanone	1.23	2740
	1.28	2810
	1.28	2900
	1.12	3030
	0.94	3110
Cyclopentanone	1.12	2780
	1.21	2900
	1.23	3000
	1.12	3100
	0.84	3230
Cyclohexanone	1.05	2900

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(5) Engineer's Bulletin No. 53, Nov., 1939, General Electric Co.

scribed in a paper by Dr. R. N. Jones.[6] The curves for the hexanone and pentanone are in good agreement with those obtained by Herold.[7] There is a well-defined fine structure in the spectra of cyclobutanone and cyclopentanone. The absorption maxima are tabulated in Table I.

In view of the spectral intensity distribution in the arc employed for illumination, the reactions in all three compounds must be caused predominantly by wave lengths around λ 2900 Å.

Vapor Pressures.—The vapor pressures of the pentanone and butanone were measured over a range of temperatures by the static method. They are given in Table II along with the vapor pressure of cyclohexanone determined by Radalescu.[8] A plot of log P against $1/T$ shows that our points lie on good straight lines. From the slopes, the heats of vaporization were calculated and these, together with the Clausius–Clapeyron constants, are given in Table III ($\log_{10} P = -(a/T) + b$).

TABLE II

P, mm.	T, °K.	P, calcd.
Cyclohexanone (Radalescu and Alexa)		
0.74	273.1	1.17
1.61	278.1	1.61
2.30	283.1	2.20
2.92	288.1	2.95
3.93	293.1	3.95
5.18	298.1	5.18
Cyclopentanone		
2.3	273.1	2.29
6.0	287.0	5.83
10.4	296.9	10.7
12.0	298.8	11.95
Cyclobutanone		
2.0	249.1	2.02
4.1	259.1	4.11
6.3	265.3	6.26
10.2	273.1	10.27
14.3	278.6	14.4
24.8	287.8	24.5
25.5	288.1	24.8
38.3	295.9	38.0
40.0	296.8	39.8
42.4	298.1	42.4
43.2	298.4	43.1

TABLE III

Compound	a	b	H_{vap} kcal./mole
Cyclohexanone	2105.0	7.7765	9.62 (Radalescu)
Cyclopentanone	2278.0	8.7020	10.41
Cyclobutanone	2008.6	8.3668	9.180

The data on cyclohexanone indicate a heat of vaporization smaller than that of cyclopentanone, which is very unlikely. Since the points of Radalescu show large deviations from the straight line, we are inclined to believe the error is in his result.

Analytical Methods.—The separation and analysis of the products have already been described by one of the present authors.[9,10] The permanent gases were analyzed by the micro methods of Blacet, Leighton and co-workers.[11–15]

Some technical changes were made in the apparatus to simplify and shorten the procedure. A rack and pinion device was substituted for the screw arrangement used by Blacet to raise and lower the mercury reservoir and an all-glass buret was made using a graduated capillary sealed into a Pyrex jacket. Analyses were reproducible to within 0.5–2%, the combustion giving the most reliable results.

The hydrocarbons were analyzed by both gas analysis and by determination of their physical properties (*i. e.*, molecular weight, vapor pressures, densities, boiling points). Confirmatory analyses were made in the higher boiling hydrocarbons to determine their olefin content. This was done by micro-titration of the samples with a solution of bromine in glacial acetic acid. These methods are all described in detail in the previously mentioned papers.[9,10]

The polymer obtained from the photolysis of cyclohexanone was shown to be cyclohexenylcyclohexanone, both by a micro-combustion analysis and by a molecular weight determination. The latter consisted of determining the freezing point depression by the polymer dissolved in ethylene dibromide and gave results good to about 10%. The water which results from this condensation was identified by the described methods, together with the fact that it turned anhydrous copper sulfate blue. None of the other substances present produced this effect.

Results of the Photolysis.—The collected data from the photolysis are given in Tables IV, V, VI.

TABLE IV

CYCLOHEXANONE

P_m	Cond., °C.	Therm., °C.	CO	C_X	C_5	P, mg. %
72	65	140	7.23	0.13, 0.9%	6.43, 89%	13, 45%
75	52	155	6.34	?	?	64, 250%
23	42	102	1.78	.31, 9.4%	1.61, 90%	3, 42%
50	49	225	4.66	.14, 1.5%	3.66, 79%	1, 5%
65	47	316	6.17	.15, 1.2%	4.89, 79%	3, 12%
60	73	125	1.84	?	1.53, 84%	30, 410%
169	99	325	8.39	.31, 1.9%	7.90, 94%	21, 63%

In all these tables, column 1 gives the arithmetical mean pressure (P_m). Column 2 gives the temperature of the condenser; column 3 the temperature of the exposed gases, as determined by a copper–constantan thermocouple. In column 4 are expressed the number of cubic centimeters at N. T. P. of carbon monoxide, produced in the run. C_X in Table IV gives the number of cubic centimeters at N. T. P. of ethylene and propylene found, the next figure being their amount relative

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[6] Jones, THIS JOURNAL, **62**, 148 (1940).

[7] Herold, *Z. physik. Chem.*, **B18**, 265 (1932).

[8] Radalescu and Alexa, *Bull. Soc. Chem. Romania*, **20A**, 89 (1938).

[9] Benson, *Ind. Eng. Chem., Anal. Ed.*, **13**, 502 (1941).

[10] Benson, *ibid.*, in press.

[11] Blacet and Leighton, *ibid.*, **3**, 276 (1931).

[12] Blacet and MacDonald, *ibid.*, **6**, 223 (1934).

[13] Blacet, MacDonald and Leighton, *ibid.*, **5**, 272 (1933).

[14] Blacet, Sellers and Blaedel, **12**, 356 (1940).

[15] Blacet and Vollman, *ibid.*, **9**, 44 (1937).

carbon monoxide. C_5 is the number of cubic centimeters of C_5 hydrocarbons produced and the next figure is this amount relative to carbon monoxide. The final column P gives the weight of the polymer and its amount relative to carbon monoxide; this latter figure is based on consideration of the polymer as the dimer of cyclohexanone.

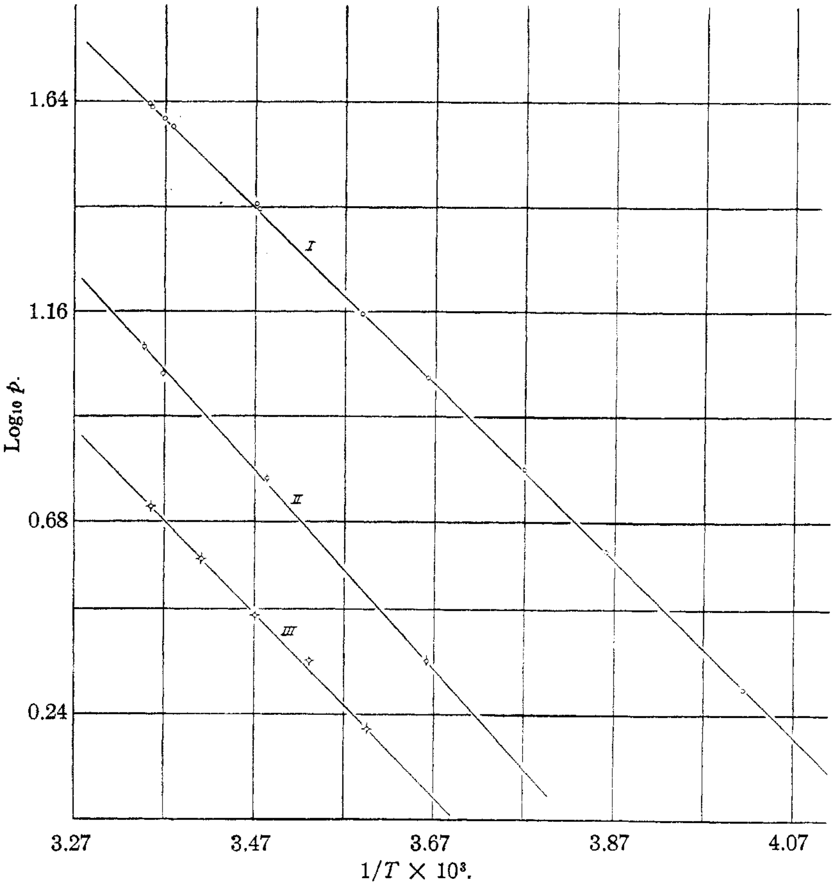


Fig. 5.—Vapor pressure curves of cyclobutanone (Curve I), cyclopentanone (Curve II) and cyclohexanone (Curve III, Radalescu).

Table V

Cyclopentanone

Run	P_m	Cond., °C.	Therm., °C.	CO	C_2H_4	C_4H_8
1	220	50	188	37.6	45.1, 60.1%	13.4, 35.6%
2	140	35	181	26.6	32.9, 62%	10.1, 38%
3	39	35	198	12.31	15.37, 61.8%	3.24, 38.0%
4	45	35	300	10.29	12.92, 62.9%	3.94, 38.3%
5	26	29	199	7.35	9.06, 61.7%	2.84, 38.6%
6	62	46	198	10.47	12.87, 61.5%	3.80, 36.3%
7	147	77	201	17.92	22.12, 61.6%	7.04, 39.3%
8	145	50	198	15.17	18.59, 61.4%	5.77, 38.0%

In Table V, the last three columns give the amounts of recovered gas, expressed in cubic centimeters at N. T. P. The percentages express these amounts in terms of the total ketone decomposition, calculated from the production of carbon monoxide.

The last column of Table VI, F_3, represents the fraction consisting of propylene and ketene. These two, which boil 6° apart, could not be fractionated, and so they were measured together. This last column gives, in effect, the cubic centimeters of ketone decomposed since no other reactions were observed. The percentages given in the other columns represent the proportions of the other products measured in terms of the last column.

In the decomposition of cyclohexanone there were actually two polymers observed. One, which had a vapor pressure of about 0.1 mm. at 25° and which was analyzed as cyclohexenylcyclohexanone, was the major part of the residue. The remainder was a non-volatile, tan-colored polymer which was found in too small quantities to be analyzed.

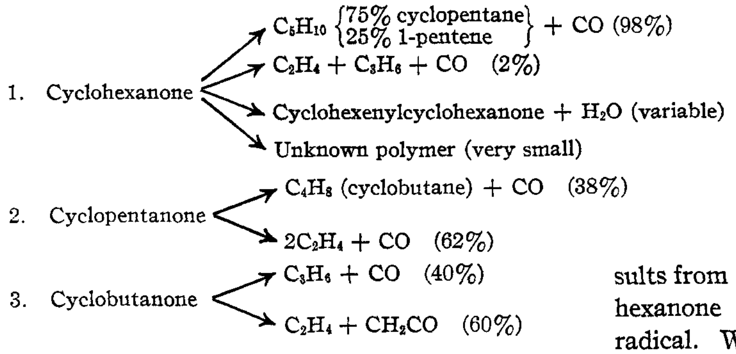
From the data in Table IV it can be seen that the production of the cyclohexenylcyclohexanone, relative to the rest, increased as the pressure increased and decreased as the temperature increased, but the ratios of the quantities of the gaseous products remained invariant with temperature and pressure in all of the decompositions.

Table VI

Cyclobutanone

Run	P_m	Cond., °C.	Therm., °C.	CO	C_2H_4	F_3
1	90	33	168	10.39, 40.9%	15.03, 59.1%	25.42
2	90	33	250	9.16, 40.9%	13.62, 59.8%	22.78
3	90	32	324	8.05, 39.1%	12.53, 60.9%	20.55
4	40	13	186	3.24, ?	?	?
5	212	57	193	12.19, 38.8%	19.13, 61.0%	31.40

Because of the different experimental conditions, a direct comparison with Norrish's results is not practicable, but it can be noted that the ratios of the gaseous products observed are quite close to those obtained by him. The results obtained here can be summarized as



It can be seen that the photolysis of cyclohexanone is much more complex than the simple reaction postulated by Norrish.[1,2]

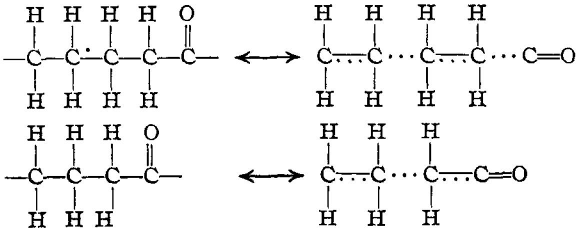
Discussion

The results of the photolysis might be interpreted as indicating that the primary process does not lead to free radicals but to an immediate fission into ultimate particles. This view, however, is not consistent with the formation of 1-pentene and of the polymer in the cyclohexanone reaction, and is certainly not in agreement with the results of photolysis of the aliphatic ketones. Gorin,[16] and more recently Taylor,[17] have shown that the decomposition of the aliphatic ketones leads to the formation of free radicals. A more plausible mechanism which is consistent with the present results is to assume that the primary process leads to the formation of polymethylene-acyl diradicals $—(CH_2)_n—\overset{|}{C}=O$. These can now undergo ring closure to the original ketone, react with another molecule of ketone to give, eventually, an aldol condensation product (*e. g.*, as in the formation of cyclohexenylcyclohexanone) or to split further.

The relative probability of this secondary decomposition, as well as the nature of the fission products obtained, can be understood from a unified point of view by the consideration of electronic (resonance) rearrangement in the intermediary diradicals. Thus in the pentamethylene-acyl diradical the only rearrangement possible is the breaking of the bond between the carbonyl group and the adjacent carbon atom, assisted by the formation of the resonating electronic structure of carbon monoxide. As is known from the study of the decomposition of aliphatic ketones, this rearrangement does not occur very rapidly and therefore the pentamethylene-acyl diradical is relatively stable, as is evidenced by the formation of the dimerization product. The dependence of the yield of the latter upon pressure and temperature suggests that the lifetime of the diradical is reduced by increasing the temperature, just as is that of the acetyl radical, and that the formation of the cyclohexenylcyclohexanone results from a reaction of the diradical with a cyclohexanone molecule, rather than with another radical. Whether a reformation of cyclohexanone occurs to any measurable extent, we are unable to say because the quantum yield has not been measured.

Both the tetramethylene-acyl diradical and the trimethylene-acyl diradical offer further possibilities for electronic resonance, which evidently increase the rates of their secondary decomposition so much that no measurable reaction with ketone molecules takes place, as shown by the absence of high molecular weight products.

These electronic rearrangements are represented on the following scheme and account for the formation of ethylene from cyclopentanone and of ketene and ethylene from cyclobutanone:



In addition to these reactions we have, of course, the same splitting off of carbon monoxide as occurs with cyclohexanone. The resulting polymethylene diradicals either close the ring or rearrange into an olefin with a shift of a hydrogen atom. The work of Bawn, *et al.*,[18,19] who studied the action of sodium vapor on alkyl dihalides and obtained products similar to those now observed, shows that cyclopropane results from trimethylene diradical, a point which we were not able to prove because of the presence of ketene. We find, thus, the seemingly strange result that those diradicals which form highly strained three- and four-membered rings do so quantitatively, whereas pentamethylene diradical rearranges into pentene-1 to a considerable extent. The difficulty, however, is only an apparent one and is resolved by a consideration of the geometry of the intermediary

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[16] E. Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

[17] May, Taylor and Burton, THIS JOURNAL, **63**, 249 (1941).

[18] Bawn and Hunter, *Trans. Faraday Soc.*, **34**, 608 (1938).

[19] Bawn and Milstead, *ibid.*, **35**, 889 (1939).

"activated" complexes. To form pentene-1, the pentamethylene diradical must momentarily form a five-membered ring involving one of the beta hydrogen atoms. This ring is slightly more strained than is the five-membered homocyclic ring leading to cyclopentane formation because of the shorter carbon–hydrogen bond distances. However, in the five-membered rings the strain is not large and hence both activated complexes may involve comparable activation energies, as evidenced by comparable yields of pentene-1 and of cyclopentane. In contrast to this, tetramethylene and trimethylene diradicals must form either four- or three-membered rings involving beta hydrogen to rearrange into corresponding olefins. The absence of these olefins among the products suggests that such rings involve much larger strain and hence larger activation energies than homocyclic rings with the same total number of atoms.

These considerations are offered in a preliminary manner and it is hoped that further and more quantitative work will test them adequately.

Summary

Cyclohexanone, cyclopentanone and cyclobutanone have been prepared and their absorption spectra and vapor pressures measured. The ketones have been subjected to photochemical decomposition in a flow system and the products analyzed, runs being made over the temperature range 150–350° and the pressure range 30–200 mm.

It has been found that the ratio of the quantities of gaseous products formed is independent of both the temperature and the pressure. Condensation products were formed only in the case of cyclohexanone and the quantity of these products depends on both temperature and pressure.

The data have been correlated with other data and a consistent hypothesis suggested as to the nature of the intermediates. The primary process is presumed to be absorption of light with the splitting of one bond and the formation of a polymethylene diradical. The previous work of Norrish is shown to be open to experimental criticism and errors in his data are explained.

The photolysis of cyclopentanone suggests a convenient method for the synthesis of cyclobutane.

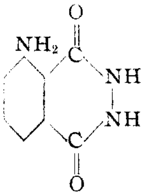
CAMBRIDGE, MASS. RECEIVED OCTOBER 24, 1941

[CONTRIBUTION NO. 255 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

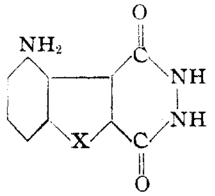
The Synthesis of 5-Aminocoumarone-2,3-dicarboxylic Acid Cyclohydrazide. A Heterocyclic Analog of 4-Aminophthalhydrazide

BY ERNEST H. HUNTRESS AND WILLIAM M. HEARON[1,2]

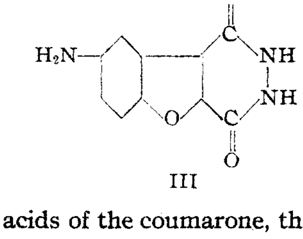
In connection with studies of the influence of structure upon the chemiluminescence observed during the oxidation of "Luminol" (I)[3] more information regarding the effect of interposition of another ring between the carbocyclic nucleus carrying the amino group and the heterocyclic cyclohydrazide ring was desired. The most desirable compounds for this purpose would possess the structure II (X = O, S, or =NH).



I



II



III

Such cyclohydrazides should be readily preparable from appropriately substituted nitro-2,3-dicarboxylic acids of the coumarone, thionaphthene, or indole series. Unfortunately, however, not one of these nitro acids has been reported.

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[1] This paper is constructed from part of a dissertation submitted in June, 1940, by Dr. Hearon to the Faculty of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[3] Huntress, Stanley and Parker, *J. Chem. Education*, **11**, 142–145 (1934).