

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Isomerization in the Photolysis of Alkyl Iodides<sup>1,2</sup>BY CHARLES E. MCCAULEY,<sup>3</sup> WILLIAM H. HAMILL AND RUSSELL R. WILLIAMS, JR.

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Liquid samples of *n*-propyl, isopropyl, *t*-butyl and isobutyl iodides were photolyzed, mostly with the 2537 Å. mercury line. From each of the first three iodides, the gaseous products were essentially equimolar mixtures of the corresponding alkane and alkene; isobutyl iodide gave anomalous results. Tracer experiments with I<sup>131</sup> show extensive photoisomerization of *n*-propyl to isopropyl iodide, especially at low temperature or short wave length. This isomerization is strongly inhibited by oxygen. Mechanisms for the various reactions are discussed and it is concluded that the isomerization is probably to be attributed to the production of HI as an intermediate in the photolysis, rather than to an intra-radical shift of hydrogen. This interpretation is supported by the production of considerable amounts of isopropyl iodide from the photolysis of ethyl iodide in the presence of propylene.

Many homogeneous thermal and photochemical reactions clearly involve free radical intermediates and although carbon-to-carbon isomerizations analogous to those observed with carbonium ions have been unambiguously demonstrated in a few large radicals such as neophyl, the behavior of small alkyl radicals is not so clear. Thermal isomerization of *n*-propyl bromide to isopropyl bromide,<sup>4</sup> slight photochemical isomerization of isobutyl to *t*-butyl iodide,<sup>5</sup> and production of di-*n*-propylmercury in photolysis of diisopropyl ketone with mercury<sup>6</sup> have been reported. On the other hand, Kharasch, Kane and Brown,<sup>7</sup> after refluxing *n*-butyryl peroxide in carbon tetrachloride, were able to isolate a substantial amount of *n*-propyl chloride but no isopropyl chloride; similarly, from the decomposition of isobutyryl peroxide in carbon tetrachloride they isolated isopropyl chloride but no *n*-propyl chloride. Brown and Russell<sup>8</sup> have found little or no isomerization in chlorination of isobutane at -15°. Experiments on thermal exchange of *n*-propyl or isopropyl iodide with iodine at 95° also fail to indicate isomerization.<sup>9</sup>

This investigation has been concerned with the question of isomerization in the photolysis of propyl iodide and in the course of the work we have also investigated the gaseous products formed in this and similar processes.

## Experimental

**Purification of Alkyl Iodides.**—The compounds were distilled at reduced pressure in a 4-foot helix-packed all-glass fractionating column, at a reflux ratio of 20/1., with a take-off of 2-4 ml./hr., preserving only the middle third. The efficiency of the column was tested by adding to one 500-g. charge of isopropyl iodide, 30 g. of I<sup>131</sup>-labeled ethyl iodide. After fractionation the isopropyl fraction showed a barely detectable activity corresponding to less than 0.01% ethyl iodide contamination.

**Preparation of Sample for Photolysis.**—Aqueous KI containing I<sup>131</sup> was evaporated to dryness in a Pyrex tube, and the residue covered with powdered K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and a plug of glass wool. The tube was then attached to the vacuum sys-

tem and pumped down, the dichromate was melted with a gas flame and the iodine produced was collected in the bottom of a tube chilled in liquid nitrogen. Five ml. of the alkyl iodide and a small amount of P<sub>2</sub>O<sub>5</sub> were then added to the tube containing I<sub>2</sub><sup>131</sup>, and covered with a plug of glass wool. The tube was frozen with liquid nitrogen, evacuated, degassed by repeated freezing, pumping and thawing, and finally distilled into the photolysis cell, a cylinder 150 × 13 mm., which was then sealed off.

**Procedure for Photolysis.**—In most of the experiments reported here, the sample was irradiated with the full light from a Hanovia Sc2537 low pressure mercury discharge tube in the form of helix. This lamp gives almost all of its light in the 2537 Å. resonance line, with the rest divided between the visible and the 1849 Å. line. For these experiments the photolysis cell was of quartz. In one experiment it was desired to exclude the 1849 Å. radiation, and a photolysis cell was constructed of Corning 7910 glass. In all runs the photolysis cell, with the vapor space screened with wrappings of black paper, was placed in the center of the helix; in this position, the sample absorbed ca. 10<sup>18</sup> quanta/min. The temperature was kept approximately constant to 30° by blowing a stream of compressed air through the lamp assembly. The usual irradiation time was 4-6 min. for samples containing I<sup>131</sup>; this permitted about 50% conversion of activity to the organic substance. When gas was to be collected, the irradiation time was 40 minutes; this made possible the collection of ca. 10<sup>-4</sup> mole of gaseous products.

In a few runs at low temperature the sealed photolysis cell was immersed in an acetone-Dry Ice mixture for several minutes, then removed, wiped very quickly, and irradiated for ten seconds in the lamp helix. This was followed by alternate periods of one minute in the cold bath and ten seconds in the lamp for a total of six minutes of actual irradiation.

One run was made at 30° using a Pyrex-filtered Cd vapor lamp similar to that described by Steacie and Potvin.<sup>10</sup> The radiation absorbed from the lamp was essentially 3261 Å. Due to the weak absorption by propyl iodide in this region, and the unfavorable geometry of the sample holder, a 5-hour irradiation period was required to obtain only 10% pickup of I<sup>131</sup>.

**Analysis for Alkyl Iodide Products.**—After irradiation of the sample, a carrier mixture containing measured amounts of various alkyl iodides was admitted to the photolysis cell through a break-off. The mixture was now washed with cold dilute aqueous Na<sub>2</sub>SO<sub>3</sub> to remove I<sub>2</sub>, then twice with ice-water, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> (or occasionally P<sub>2</sub>O<sub>5</sub>), filtered and fractionated. In some preliminary experiments, the fractionation was done on a 12" Podbielniak Micro-Analyzer packed with Hastelloy "Heli-Pak." However, it was found that there was a significant amount of exchange of activity among the higher boiling fractions, most probably catalyzed by the metal iodides formed by corrosive attack on the packing. For this reason, all subsequent work including the results reported here, was done on the all-glass column described above. In this latter column, experiments showed that exchange of activity among the various alkyl iodides did not occur.

After fractionation under reduced pressure, a 1-ml. sample from the central portion of each fraction was diluted

(1) Presented at the 124th Meeting of the American Chemical Society, Chicago, September, 1953.

(2) This work was supported, in part, under Atomic Energy Commission contract AT(11-1)-38 and Navy contract Nour-06900.

(3) St. Peter's College, Jersey City, N. J.

(4) A. Michael and H. Leupold, *Ann.*, **379**, 263 (1911).

(5) P. Ramart-Lucas and F. Salmon-Legagneur, *Compt. rend.*, **186**, 39 (1928), and G. Emschwiller, *Ann. chim.*, **17**, [10], 413 (1932).

(6) H. H. Glasebrook and T. G. Pearson, *J. Chem. Soc.*, 1777 (1936).

(7) M. S. Kharasch, S. S. Kane and H. C. Brown, *THIS JOURNAL*, **63**, 526 (1941).

(8) H. C. Brown and G. A. Russell, *ibid.*, **74**, 3995 (1952).

(9) R. G. Badger, C. T. Chmiel and R. H. Schuler, *ibid.*, **75**, 2498 (1953).

(10) E. W. R. Steacie and R. Potvin, *Can. J. Research*, **16B**, 337 (1938).

to 25 ml. with hexane, and the activity was measured in a small liquid-containing tube. The product of this specific activity of a fraction by the original volume of the species used as carrier gives the total activity of the fraction. The sum of these total activities for all the measured fractions is defined as the total organic activity; from this the percentage activity appearing in a given species is calculated. The labor required to effect a clean fractionation increases very rapidly with the number of components in a mixture; for this reason, when it was known that a certain component would contain only a small amount of activity or none at all, it was sometimes omitted from the carrier mixture. In such cases the percentages reported in Table IV are still rigorously correct only if looked on as *ratios*.

**Analysis for Hydrocarbon Gases.**—In these runs, no iodine was added initially to the alkyl iodide. After photolysis, the sample tube was attached to a small concentric-tube fractionating column, topped by a cold finger containing Dry Ice, and attached to the vacuum rack. The system was then allowed to reflux for several hours, and the gaseous products periodically pumped off by a Saunders-Taylor apparatus to an evacuated bulb. Samples from this bulb were then analyzed on a 21-103A Consolidated mass spectrometer.

**Check on Validity of Iodine-tracer Method.**—The amount of material actually decomposed during a normal photolysis is extremely small, and some questions concerning the carrier technique have been raised.<sup>11</sup> An examination of the main possibilities of error in the present investigation seems to indicate that considerable reliability may be claimed for the results.

(a) The column used has good fractionation efficiency, as evidenced by the results quoted under purification of materials, and by the fact that redistillation of active fractions from inactive alkyl iodides of higher and lower boiling point did not change the specific activity of the active fractions.

(b) No significant thermal exchange of activity between various component iodides has been found in the all-glass column. This was tested as follows. A mixture was made of several inactive alkyl iodides and one active iodide, and refluxed gently for six hours, then fractionated; the pressure was adjusted, when necessary, so that the temperature never rose above 75°. The results are shown in Table I.

TABLE I

## TEST OF THERMAL EXCHANGE

EtI, %	<i>i</i> -PrI, %	<i>n</i> -PrI, %	<i>i</i> -BuI, %	<i>t</i> -BuI, %
0.0 <sup>a</sup>	0.2	99.8 <sup>b</sup>	...	...
99.99 <sup>b</sup>	0.01	...	...	...
0.0	..	...	99.7 <sup>b</sup>	0.3
0.2	..	...	0.5	99.3 <sup>b</sup>

<sup>a</sup> Methyl iodide was also used as a carrier, and also showed zero activity. <sup>b</sup> Original active fraction. <sup>c</sup> Leaders indicate component not used in mixture.

(c) During the washing with Na<sub>2</sub>SO<sub>3</sub> of the carrier-iodine mixture after photolysis, a small amount of exchange is to be expected because of attack by I<sup>-</sup> ions on the alkyl iodide molecules. Mixtures of inactive methyl, isopropyl and *n*-propyl iodides were therefore made in the amounts normally used for a carrier run, I<sub>2</sub> containing I<sup>131</sup> was added, then removed with aqueous Na<sub>2</sub>SO<sub>3</sub> and samples of the organic phase and water phase were counted. Two such tests showed transfer to the organic phase of only 0.4 and 0.7% of the total activity. When a complete blank, including a four hour degassing period, was run on *n*-propyl iodide, the organic phase was found to contain 2.3% of the total activity, and fractionation showed that this was partitioned as follows: isopropyl, 0.1%; *n*-propyl, 1.9%; excess activity in stillpot residue, 0.3%. This small activity in the *n*-propyl fraction is probably due to a combination of slow thermal exchange with iodine and a small amount of photolysis caused by some fairly short-wave component of the laboratory illumination.

*t*-Butyl iodide was found to behave in a highly exceptional manner. Iodine containing I<sup>131</sup> was added to *t*-butyl iodide in a Pyrex vessel under less than normal laboratory

illumination, shaken for two minutes, washed with Na<sub>2</sub>SO<sub>3</sub>, dried and counted. In each of two tests, over 66% of the activity was found in the *t*-butyl iodide. This result is not due to ionic attack during the washing, since shaking *t*-butyl iodide for two minutes with a cold aqueous solution of NaI<sup>131</sup> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> resulted in the transfer of only 0.3% of the activity to the organic phase. The reasons for this behavior are not completely understood, but it was evidently necessary to exclude *t*-butyl iodide, in general, from carrier experiments. It may be conjectured that the reaction is due to attack on *t*-butyl iodide molecules by iodine atoms.

## Results

**Gaseous Hydrocarbon Products.**—All of the photolyses discussed in this section were done at 30° in the full light of the mercury lamp. The mass analyses of the gas produced in the photolysis of *n*-propyl and isopropyl iodide are shown in Table II; these data agree fairly well with those reported by Emschwiller.<sup>5</sup>

TABLE II  
COMPOSITION OF GAS PRODUCTS

RI	H <sub>2</sub> , %	C <sub>2</sub> H <sub>4</sub> , %	C <sub>2</sub> H <sub>6</sub> , %	C <sub>3</sub> H <sub>8</sub> , %
<i>n</i> -Propyl	0.4	0.8 <sup>a</sup>	47.5	51.4
<i>n</i> -Propyl	0.2	0.7 <sup>a</sup>	47.8	51.3
Isopropyl	.. <sup>b</sup>	0.0	51.2	48.8

<sup>a</sup> Although small, the ethylene content was shown to be real by subsequent low temperature fractionation. <sup>b</sup> Not measured.

According to our results, the gas production in the photolysis of *t*-butyl iodide follows the same pattern as *n*-propyl and isopropyl iodide. For all three substances the mass analyses were extremely clean, with all residuals essentially zero. However, as Table III shows, our results are in complete disagreement with those reported by Emschwiller.<sup>5</sup> We have no explanation of this discrepancy.

TABLE III

COMPOSITION OF GAS FROM PHOTOLYSIS OF *t*-BUTYL IODIDE, %

	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub>
Emschwiller <sup>5</sup>	23	12	47	18	0
This investigation	H <sub>2</sub>	CO <sub>2</sub>	<i>i</i> -C <sub>4</sub> H <sub>8</sub>	<i>i</i> -C <sub>4</sub> H <sub>10</sub>	Other
	0.3	0.2	51.5	48.1	0.0

The gas produced in the photolysis of isobutyl iodide was a very complex mixture, and despite all efforts, we were unable in the analysis to achieve a completely satisfactory set of residuals. A repetition of the experiment with a freshly distilled batch of isobutyl iodide<sup>12</sup> gave approximately the same results. The gas consisted of nearly equal amounts of alkanes and alkenes, but while the alkane was almost entirely isobutane, as expected, the major part of the alkene was 2-butene with only a small contribution from isobutylene. Isobutyl iodide thus seems to constitute a distinct anomaly. Only a limited comparison can be made between our data and those of Emschwiller, since his method of analysis permitted no distinction to be made between isomers; it can only be said that his results with isobutyl iodide do not disagree with ours.

**Results of Tracer Experiments.**—Table IV summarizes the distribution of product alkyl iodides

(11) M. S. Kharasch, W. Zimmt and W. Nudenberg, *J. Chem. Phys.*, **20**, 1659 (1952).

(12) The authors are indebted to Mr. David Bunbury for making the run, and to Mr. George Young for the mass analysis.

TABLE IV  
 DISTRIBUTION OF I<sup>131</sup> ACTIVITY AFTER PHOTOLYSIS

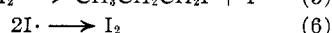
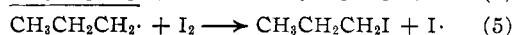
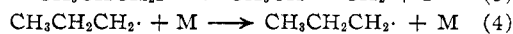
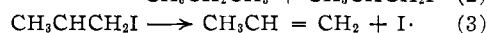
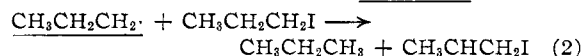
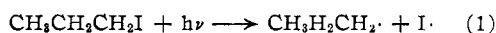
Iodide photolyzed	$\lambda$ (Å.)	Temp., °C.	Initial $M$ $I_2 \times 10^3$	Air content	MeI, %	EtI, %	<i>i</i> -PrI, %	<i>n</i> -PrI, %	Excess in still. pot
<i>n</i> -Propyl	3261	30	3	Air-free	.. <sup>a</sup>	..	2.8	97.2	+9.0
<i>n</i> -Propyl	2537	30	4	Air-free	..	..	19.9	80.1	0.0
<i>n</i> -Propyl	2537 + 1849	30	8	Air-free	0.8	0.3	28.3	70.7	...
<i>n</i> -Propyl	2537 + 1849	30	3	Air-free	1.0	0.2	27.8	71.7	...
<i>n</i> -Propyl	2537 + 1849	30	3	Air-sat.	2.9	0.0	2.0	95.1	+0.4
<i>n</i> -Propyl	2537 + 1849	30	5	Air-sat.	2.0	..	3.1	94.9	-2.0
<i>n</i> -Propyl	2537 + 1849	-70	14	Air-free	0.6	..	58.6	40.8	-1.0
<i>n</i> -Propyl	2537 + 1849	-70	3	Air-free	..	..	60.1	39.9	+0.6
Isopropyl	2537 + 1849	30	3	Air-free	0.2	0.2	95.1	4.5	+1.5
Isopropyl	2537 + 1849	30	3	Air-free	..	..	96.1	3.9	0.0

<sup>a</sup> Leaders indicate substance not included in carrier mixture.

resulting from the photolysis of *n*-propyl and isopropyl iodides at different wave lengths and temperatures, using both air-free and air-saturated samples. The percentage of *n*-propyl iodide in the first experiment is probably somewhat too large. During the long (5 hr.) photolysis, there may have been a significant amount of exchange caused by attack of iodine atoms on the *n*-propyl iodide molecules. The method used for calculating the percentages in Table IV has been described in the section on experimental methods.

### Discussion

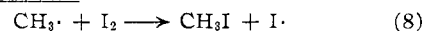
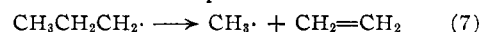
The production of substantially equivalent amounts of alkane and alkene shown in Tables II and III suggests that at least part of the reaction proceeds along the following path, similar to the one proposed for ethyl iodide.<sup>13</sup> Underlined type indicates a hot radical, *i.e.*, one which has not yet lost by collision the large difference between the energy of the absorbed quantum and that required to break the carbon iodine bond.



Reaction 2 is the crucial part of this scheme in that it postulates that a hot propyl radical abstracts only  $\beta$ - and not  $\alpha$ - or  $\gamma$ -hydrogens from neighboring molecules. This is a little curious. Rebbert and Steacie<sup>14</sup> have shown that radical attack on a hydrocarbon chain removes a tertiary hydrogen more easily than a secondary one, and a secondary more easily than a primary, but the differences in activation energy are small, only a few kcal., and one would not expect hot radicals to discriminate between them. However, the I<sup>131</sup> experiments favor the reaction scheme given above, in that they show no sign of the fairly stable  $\alpha,\alpha$  or  $\alpha,\gamma$  diiodides that would be expected from removal of  $\alpha$ - or  $\gamma$ -hydrogens. Two possible explanations, not necessarily mutually exclusive, suggest themselves: either reaction 2 is not ele-

mentary but is the over-all result of a short chain, or, more probably, the activation energy for abstracting a  $\beta$ -hydrogen from an alkyl iodide is much smaller than is indicated by Rebbert and Steacie's results with hydrocarbons, because our equations 2 and 3 occur simultaneously as part of a single concerted reaction.

The production of ethylene is presumably due to an alternate reaction to equations 2 and 3



Reaction 7 is believed to occur in several pyrolyses and is supported here by the appearance of an appropriate amount of methyl iodide in the tracer experiments (*cf.* Table IV).

The principal facts emerging from Table IV are that the photoisomerization of *n*-propyl to isopropyl iodide (a) is a real phenomenon, and increases with decreasing wave length, (b) is very strongly repressed by the presence of air, (c) is very great at low temperatures and (d) that the specific activity of the stillpot residue is very nearly the same as that of the *n*-propyl fraction. This implies the absence of any appreciable amounts of diiodides, thus confirming equation 2.

The small activity in the ethyl fractions is most probably due to contamination by the following active fraction. The methyl activities, however, seem quite real, since on several tries they persisted unchanged upon redistillation from fresh inactive ethyl iodide. In the case of the fairly strong isopropyl activities, it was easy in several cases so to proportion the amounts of carriers that the isomerized product showed a *specific* activity equal to or higher than the parent compound.

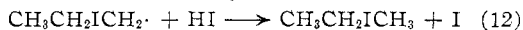
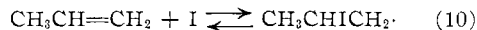
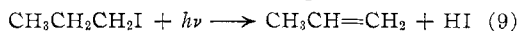
**Effect of Air.**—We assume that the repression of isomerization noted in photolyses conducted in air is to be attributed to dissolved oxygen. Although the solubility of oxygen in alkyl iodides is not known, estimation from values for other organic liquids indicates an oxygen concentration of approximately  $2 \times 10^{-3}$  molar for air-saturated *n*-propyl iodide at 30°. Hence in the experiments of Table IV the iodine concentration is about twice the oxygen concentration. Now while the quantum yield for iodine production is not a function of iodine concentration in air free photolyses (one of the main facts leading to the proposal of a hot radical mechanism for that process) the strong dependence of isomerization efficiency on small con-

(13) W. H. Hamill and R. H. Schuler, *THIS JOURNAL*, **73**, 3466 (1951).

(14) R. E. Rebbert and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 1723 (1953).

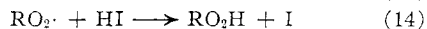
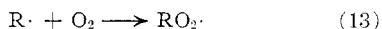
centrations of oxygen makes it evident that a hot radical mechanism will not suffice to explain this phenomenon. It is unlikely that oxygen would react so selectively with isopropyl rather than propyl radicals if these were formed in fixed proportion in the initial act or by immediately subsequent collisions.

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



The sequence of reactions 10, 11 and 12 is quite plausible once the presence of hydrogen iodide is admitted, as it is known<sup>15</sup> that iodine strongly catalyzes the addition of hydrogen iodide to propylene even at  $-78^\circ$ . 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.



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 inter-

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

mediate in such a photolysis has been subjected to partial experimental test as follows: Air-free ethyl iodide was photolyzed at  $30^\circ$ , in the full light of the mercury lamp, in the presence of  $\text{I}_2^{131}$  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.<sup>16</sup>

TABLE V  
ACTIVITY IN CARRIER FRACTIONS AFTER PHOTOLYSIS OF  
ETHYL IODIDE CONTAINING PROPYLENE

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

<sup>a</sup> 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  $2537 \text{ \AA}$ . and the obvious proximity of the  $\beta$ -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<sup>17</sup> 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  $\beta$ -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.

(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

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

## The Thermal Decomposition of Cyclopentanone<sup>1,2</sup>

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  $488$ – $543^\circ$  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  $512^\circ$ .

Although no extensive study of the thermal decomposition of cyclopentanone appears to have been published in the literature, Ibuki<sup>3</sup> has reported that cyclopentanone decomposes in the region  $530$ – $550^\circ$  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<sup>4–6</sup> involves a cleavage of the ring; the main gaseous

(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).

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