98. *Primary Photochemical Reactions. Part VI. The Photochemical Decomposition of Certain Cyclic Ketones.*

By Olive D. Saltmarsh and Ronald G. W. Norrish.

In previous papers (Norrish and Kirkbride, J., 1932, 1518; Norrish, Crone, and Saltmarsh, J., 1933, 1533; 1934, 1456; Norrish and Appleyard, *ibid.*, p. 874) an examination of the primary photochemical change suffered by the vapours of simple ketones was described. It was concluded that, when light corresponding to the absorption band of the carbonyl group lying between *ca.* 3500 and 2000 Å.U. is absorbed, two types of decomposition are possible: (I) With short-chain ketones, the change typified by the photochemical decomposition of acetone occurs: $CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow C_2H_6 + CO$. (II) With long-chain ketones, a break may occur instead in the hydrocarbon chain, as with methyl butyl ketone, which decomposes almost quantitatively according to the equation:

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \longrightarrow CH_3{\cdot}CO{\cdot}CH_3 + CH_3{\cdot}CH{:}CH_2.$$

From methyl ethyl ketone, three paraffins were produced in nearly equal amounts, and the total paraffin was nearly equivalent to the carbon monoxide, the decomposition being represented to the extent of about 90% by the equation:

$$CH_3{\cdot}CO{\cdot}C_2H_5 \longrightarrow \tfrac{1}{3}(C_2H_6 + C_3H_8 + C_4H_{10}) + CO.$$

A further study of the fluorescence and absorption of acetone confirmed our view that decomposition of the type (I) arises from a primary change in which free radicals are produced, while that of type (II) does not. These conclusions have been confirmed in a very direct manner by Pearson (J., 1934, 1718), who isolated free radicals from acetone and methyl ethyl ketone, but *not* from methyl butyl ketone. The type of primary disruption associated with type (I) is itself of particular interest, for it appears that not one but both hydrocarbon radicals are ejected as a result of the absorption of a light quantum, to leave a normal ($^1\Sigma$) molecule of carbon monoxide: *

$$CH_3{\cdot}CO{\cdot}C_2H_5 \longrightarrow CH_3 + C_2H_5 + CO - 78 \text{ kg.-cals.}$$

This follows from the equivalence of the hydrocarbons and carbon monoxide, which excludes the possibility of the polymerisation of such radicals as $\cdot CO{\cdot}C_2H_5$ and shows that, if they are formed at all, they must decompose spontaneously within a very short time.

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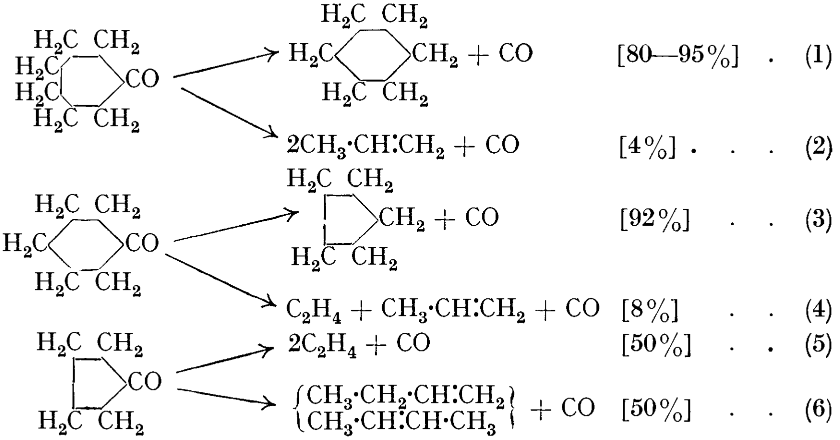
* The energy absorbed in the elimination of a single free radical corresponds to the thermal value of the C–C bond (*ca.* 89·5 kg.-cals.). To eliminate two free radicals we only require 78 kg.-cals., because the reorganisation of the carbonyl group (>CO) to carbon monoxide (C≡O) yields 101 kg.-cals. This point has already been fully discussed by one of us (Norrish, *Trans. Faraday Soc.*, 1934, **30**, 103).

The discovery of these two types of photochemical change made it of special interest to study in some detail the photolysis of cyclic ketones, for, with a ring of several carbon atoms, it is not apparent which of the two types of decomposition will intervene. Whatever the character of the reaction, however, it might be expected to throw fresh light on the mechanism of these changes.

In the present paper we examine the decomposition of *cyclo*-heptanone, -hexanone, and -pentanone. The first two give a high yield of cyclic hydrocarbon, together with a small quantity of its olefinic breakdown products, and an equivalent quantity of carbon monoxide. The last gives ethylene, isomeric butylenes, and carbon monoxide. Where a cyclic hydrocarbon of six or five carbon atoms is possible, this is readily formed, but, instead of *cyclo*butane, only its breakdown or isomerisation products are obtained.

These reactions may be summarised by the following scheme :



Hence, these cyclic ketones decompose primarily by a process of the first type, and the essential simplicity of the process affords further evidence of the simultaneous rupture of both bonds attached to the carbonyl, as has already been concluded on other grounds.

EXPERIMENTAL.

The apparatus employed was similar to that illustrated in Part IV (J., 1934, 874). 3—4 G. of the ketone were refluxed in a vacuum in a long-necked, quartz flask of 100 c.c. capacity. The attachment of the flask to the double-surface condenser was made by way of a water-cooled ground joint, lubricated by a thin film of " Apiezon " grease. The vapour in the neck at a pressure of 1—10 mm. was subjected to the full radiation of a vertical mercury-vapour lamp, while the liquid ketone was carefully protected from irradiation by covering the spherical part of the flask with asbestos paper. The gaseous products of decomposition collected mainly in a 1-litre globe, out of range of the radiation, and could be pumped off by way of a liquid-air trap and a manometer by means of a Toepler pump. The apparatus could also be evacuated by means of a " Hyvac " pump. When the irradiation was completed (3—30 hours, corresponding to the decomposition of 0·1—0·6 g. of ketone), the products were separated into three fractions by pumping off with the flask and trap cooled (1) in liquid nitrogen at — 192°, (2) in solid carbon dioxide and ether at — 78°, and (3) in ice and hydrogen chloride at — 30° or ice at 0°. The various fractions were analysed separately. Fraction (1) was practically pure carbon monoxide. Fraction (2) consisted solely of olefins, which were usually identified by explosion. Fraction (3) consisted of volatile liquids which were distilled into small weighed tubes, and these were sealed off and re-weighed. These liquids proved to be hydrocarbons, and were identified by a determination of their vapour pressures, b. p.'s, and f. p.'s. To determine their vapour pressures, they were distilled into the trap, isolated from the rest of the apparatus by a stopcock, and allowed to warm to room temperature, the pressure being read off on the manometer. The boiling points were determined by the micro-method of Smith and Menzies (*J. Amer. Chem. Soc.*, **1910**, **32**, 897) and generally found to be steady.

Materials.—(1) *cyclo*Heptanone, prepared by Mosettig and Burger's method (*ibid.*, **1930**, 52, 3456), *viz.*, addition of *cyclo*hexanone to an ethereal solution of diazomethane, was purified through its bisulphite compound and finally dried over calcium chloride; b. p. 180°.

(2) *cyclo*Hexanone was obtained by similar purification of the commercial product; b. p. 153—154°.

(3) *cyclo*Pentanone, prepared by the dry distillation of adipic acid in the presence of a small quantity of barium hydroxide ("Organic Syntheses," 1925, **5**, 37), was similarly purified; b. p. 129—130°.

Decomposition of cyclo*Heptanone.*—Since the vapour pressure of the ketone is very low, 20—30 hours' irradiation was required for the accumulation of sufficient products for satisfactory analysis. Fraction (1) consisted entirely of carbon monoxide. Fraction (2) was small in amount, and completely absorbed by bromine: it was shown by explosion to be propylene. Fraction (3) (0°) was a liquid of high vapour pressure (Found, by micro-method: C, 87·4; H, 13·9. Calc. for C_6H_{12}: C, 85·7; H, 14·3%). Its physical constants are here compared with those of *cyclo*hexane:

	Vapour pressure, mm.*			
	At 18°.	At 47°.	B. p.	F. p.
*cyclo*Hexane	74	230	81°	6·5°
Fraction (3)	77	223	77—81	3·5

A mixed m. p. gave 5·7°. The liquid was inert, immiscible with water, and unaffected by reagents. A summary of the analytical results of two experiments is given below. In the first, the maximum quantity of *cyclo*hexane was extracted by distillation; in the second, no attempt was made at quantitative separation.

Time of illumination, hrs.	Products of decomposition (converted into c.c. at *N.T.P.*).			
	Total.	Fraction (1). CO.	Fraction (2). C_3H_6.	Fraction (3). C_6H_{12}.
34	69·3	32·7	2·7	24
23	30·1	21·6	0·5	8

According to the equations (1) and (2), the volume of carbon monoxide formed in the decomposition should be equal to that of the *cyclo*hexane plus half that of the propylene. In the first experiment, therefore, this should be 25·35 c.c., as compared with 32·7 c.c. found; this deficiency, however, is not surprising in view of the difficulty of fractionating the last traces of *cyclo*hexane from the unchanged *cyclo*heptanone. Since the yield of propylene fixes the amount of ketone which decomposes according to equation (2), the proportions of the two directions of breakdown are calculated to be as shown on p. 456.

Decomposition of cyclo*Hexanone.*—After irradiation of the vapour of the ketone for 4—5 hours, the gaseous products were pumped off in three fractions at the same temperatures as before. Fraction (1) consisted of pure carbon monoxide; (2) was completely absorbed by bromine water, and was shown by explosion to consist of equal volumes of ethylene and propylene; (3) consisted of a liquid of high vapour pressure, which was distilled off and weighed (f. p. −95·5°, b. p. 49·5—50·5°, whereas the data recorded for *cyclo*pentane are −93·3° and 49·5°). The liquid was immiscible with water and quite inert to all reagents. In accordance with the rest of the analytical data, there is no doubt as to its identity with *cyclo*pentane. A summary of the analytical results is given:

Time of illumination, hrs.	Products of decomposition (converted into c.c. at *N.T.P.*).			
	Total.	Fraction (1). CO.	Fraction (2). $C_2H_4 + C_3H_6$.	Fraction (3). *cyclo*Pentane.
4	207·3	98·9	17·3	91·0
4·5	208·3	118·2	15·1	75·0

According to the equations (3) and (4), the volume of carbon monoxide should be equal to that of *cyclo*hexane plus half the total olefins. For the first experiment, this should be 99·65 c.c. (cf. 98·9 c.c.); in the second experiment no attempt was made to obtain a quantitative yield of *cyclo*pentane, the liquid being fractionated several times in the decomposition apparatus in order to ensure its absolute purity for the determination of b. p. and f. p. This accounts for the deficiency. It is apparent that about 90% of the decomposition followed equation (3) while 8—9% followed equation (4).

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* For the determination at 47° the connecting tubing and manometer were heated to 60° by winding them with a nichrome wire and asbestos wool, and passing a suitable current. The trap containing the liquid was then heated to 47° by a bath.

Decomposition of cyclo*Pentanone.*—The analysis of the products proved somewhat more complicated in this case. In view of the previous results, it was expected that some *cyclo*butane might be formed, but none was found; instead, there resulted a considerable quantity of butylene, which was isolated partly as gas, and partly as liquid.

The ketone was irradiated for 3—5 hours, and the products separated as before. Fraction (1) was pure carbon monoxide. Fraction (2) was completely absorbed by bromine water, and shown by explosion to be a mixture of ethylene with some higher olefinic hydrocarbons. In order to identify the latter, the gas was allowed to expand into a dry bulb cooled in a freezing mixture, and its pressure–volume isothermals determined at temperatures from 0° to — 20°. The gas contained a constituent condensable at — 20° and having a vapour pressure of about 250 mm. at this temperature. The b. p. of Δ^{β}-butylene is 1·4°, and the vapour pressures of both ethylene and propylene are of the order 200 mm. at temperatures 20° below their b. p.'s; thus we may assume that the vapour pressure of Δ^{β}-butylene, which is not recorded in the literature, will be of the order 200 mm. at — 20°, and this compound probably forms a considerable constituent of fraction (2).

A liquid of high vapour pressure remained in the quartz flask after the gaseous products had been removed, and was separated as fraction (3) by distillation from the unchanged *cyclo*pentanone at — 20°. The vapour density of the liquid was determined by measuring the pressure of the unsaturated vapour in a part of the apparatus of known volume, and then condensing it into a small previously weighed tube attached to the apparatus by a rubber joint, sealing off, and weighing. The vapour density determined in this way in two experiments was 23·7 and 27·5 (Calc. for $C_4H_8 : 28$). Part of the liquid was next allowed to evaporate into a gas burette, and treated with bromine water, over 95% being absorbed instantaneously. *cyclo*Butane does not react with bromine water (Willstätter and Bruce, *Ber.*, 1907, **40**, 3988), and we therefore conclude that the product is a butylene. Its m. p., — 96°, was between that of Δ^{α}- and Δ^{β}-butylene (— 130° and above — 78° respectively), and it may therefore be taken to be a mixture of these isomerides, the presence of butylene in fraction (2) being due to the volatility of the liquid, which is still unfrozen at — 78°.

The analysis of the products of decomposition was:

Time of irradiation, hrs.	Volumes of products (converted into c.c. at *N.T.P.*).				
	Total.	Fraction (1). CO.	Fraction (2). C_2H_4.	C_4H_8 (gas).	Fraction (3). C_4H_8 (liquid).
4	106	39·5	66·6		6·05
5*	358·5	152	122·5	65·5	17·5
4·5	136	51·4	62·2	15·6	6·8

* A greater intensity was used in this experiment.

According to the equations (5) and (6), the volume of carbon monoxide should be 144·2 and 53·5 c.c. in the second and the third experiment, respectively (Found: 152, 51·4 c.c.); the agreement is thus satisfactory. It will be seen that butylene and ethylene are formed approximately in the ratio 1 : 2, and that therefore each of the two reactions is equally probable.

DISCUSSION.

The type of decomposition thus found for the simple cyclic ketones agrees well with that found for short-chain, open ketones. There is no tendency for a *primary* rupture of the hydrocarbon part of the ring, similar to that occurring with long-chain, open ketones. In this case, however, the possibility of eliminating a molecule of acetone cannot be visualised without the creation of acetylenic hydrocarbons. In conformity with the decomposition of simple mixed ketones, we see that the carbon monoxide must be eliminated as a result of the simultaneous or nearly simultaneous rupture of both links, for there is no tendency to any polymerisation of heavy radicals, and the carbon monoxide is equivalent to the hydrocarbons produced.

It is notable that, although the two higher cyclic ketones each gave about 90% decomposition to the lower *cyclo*paraffin together with a small amount of olefin, yet *cyclo*pentanone yielded no detectable *cyclo*butane, but gave butylene and ethylene instead. This difference is explained by the different stabilities of the *cyclo*paraffins, the heat effects for the reactions $[CH_2]_nCO \longrightarrow [CH_2]_n + CO$ being calculated from established thermal data to be 31·5, 33·6, and — 2·2 kg.-cals. for $n = 6, 5$, and 4 respectively. It is therefore seen that the reactions are either considerably exothermic, or thermoneutral. The magnitude of the light quantum is of the order 100 kg.-cals. per g.-mol., and this amount of energy plus the heats of reaction must appear in the products. Hence, it is probable that the cyclic paraffins will be liberated in a high state of thermal vibration. We may conclude that this thermal energy is sufficient entirely to decompose or isomerise the unstable *cyclo*butane (or to prevent its ever being formed), while the two higher homologues are nearly proof against its disruptive effects : even here, however, some 5% of the cyclic hydrocarbons are decomposed to olefins. It is not possible to generalise further about the various types of photochemical decomposition exhibited by ketonic substances. Preliminary experiments upon other typical ketones indicate that the full range of possibilities has not yet been disclosed. It may be affirmed, however, that the remarkable simplicity and variety attending these and analogous decompositions make the photochemistry of the carbonyl group a study of fundamental importance.

SUMMARY.

The photodecomposition of the vapours of *cyclo*-heptanone, -hexanone, and -pentanone has been studied in the full light of the mercury lamp. The ketones absorb between 3500 and 2000 Å.U. The equations summarising the results are given on p. 456.

In accordance with previous work, the primary change is conceived as a simultaneous or nearly simultaneous rupture of the two bonds joining the carbonyl group to the ring, carbon monoxide being eliminated. Since all the changes are themselves either exothermic or thermoneutral, the energy of the light quantum must appear in the products. As a result, it is suggested that thermal vibrations appear in the hydrocarbon ring, which result in the slight decomposition of the *cyclo*hexane and *cyclo*pentane to olefins, and the almost complete decomposition or isomerisation of the *cyclo*butane.

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