287. *Primary Photochemical Reactions. Part X. The Photolysis of Cyclic Ketones in the Gas Phase.*

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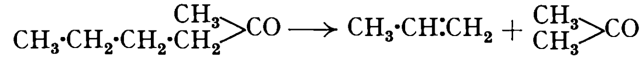
The photolysis of the following cyclic ketones in the vapour phase has been studied: *cyclo*hexanone, suberone, 2-, 3-, and 4-methyl*cyclo*hexanones, menthone. *cyclo*Hexanone and suberone were found to decompose by Type I reactions, yielding carbon monoxide and olefins rather than carbon monoxide and the corresponding cyclic hydrocarbons as previously reported by Saltmarsh and Norrish. The origin of this discrepancy was sought in a variation of the nature of the hydrocarbon with temperature of decomposition without success. It is possible that it may depend on wave-length, but this was not elucidated. It is notable that Bawn and Hunter found that the trimethylene diradical yields a mixture of *cyclo*propane and propylene. 3- and 4-Methyl*cyclo*hexanones also decompose mainly according to Type I, but in addition a new type is found, resulting in the production of a diolefin and an aldehyde. Where possible, a simple Type II decomposition occurs: this is even the case with 2-methyl*cyclo*hexanone, the primary products of the Type II reaction being methylene radicals and *cyclo*hexanone. Menthone decomposes almost exclusively according to Type II, forming propylene and 3-methyl*cyclo*hexanone. The similarity of the Type II reaction undergone by these cyclic ketones to that exhibited by the straight-chain carbonyl compounds is strong evidence against the participation of free radicals in this type of reaction.

The present paper extends our study of the photolysis of the vapours of aldehydes and ketones with an investigation of the products of decomposition of cyclic ketones in the vapour phase. Previous work (Norrish and Kirkbride, J., 1932, 1518; Norrish, Crone, and Saltmarsh, J., 1933, 1533; 1934, 1456; Norrish and Appleyard, *ibid.*, p. 874; Bamford and Norrish, J., 1935, 1504) has shown that there are two main types of decomposition undergone by carbonyl compounds. Type I consists in a unimolecular elimination of carbon monoxide with production of saturated hydrocarbons, and may be represented approximately by the following equations:

$$\left.\begin{array}{ll}\text{For aldehydes: } & \text{R·CHO} \longrightarrow \text{RH} + \text{CO} \\ \text{For ketones: } & \text{R·CO·R}' \longrightarrow (\text{R}_2 + \text{RR}' + \text{R}'_2) + \text{CO}\end{array}\right\} \quad . \quad . \quad . \quad (1)$$

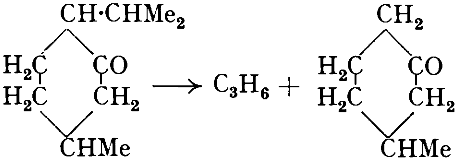
Type II, on the other hand, leads to the formation of an olefinic hydrocarbon together with a simpler carbonyl compound as a result of the cracking of the hydrocarbon chain between the α- and the β-carbon atom. This reaction appears to be of general occurrence with the higher carbonyl compounds; *e.g.*, with methyl *n*-butyl ketone:



$$\begin{matrix}CH_3\\CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2\end{matrix}{>}CO \longrightarrow CH_3{\cdot}CH{:}CH_2 + \begin{matrix}CH_3\\CH_3\end{matrix}{>}CO \quad . \quad . \quad . \quad (2)$$

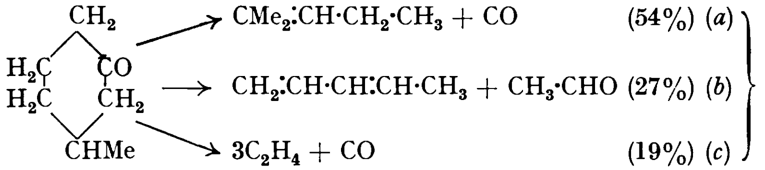
The following compounds are studied in this paper: *l*-menthone; 2-, 3-, and 4-methyl*cyclo*hexanones; *cyclo*hexanone and *cyclo*heptanone (suberone).

The investigation began with the study of *l*-menthone which, in view of its structure, provided an interesting test case for comparing the relative probabilities of the decompositions of Type I and Type II, for it had previously been found (Saltmarsh and Norrish, J., 1935, 1504) that *cyclo*hexanone itself decomposes nearly exclusively (92%) by the former mechanism, yielding carbon monoxide and *cyclo*pentane. With menthone it was found that this decomposition gives place almost completely to the alternative Type II, the products being propylene and 3-methyl*cyclo*hexanone:



. . . . . (3)

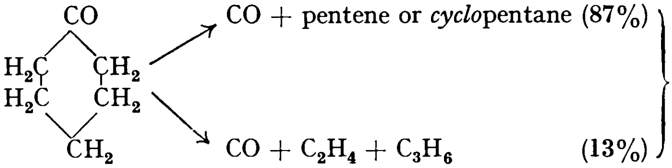
The subsequent photolysis of the 3-methyl*cyclo*hexanone which occurred, however, made it necessary to study the decomposition of this substance in detail, and thereupon unexpected differences between 3-methyl*cyclo*hexanone and the previous results for *cyclo*hexanone came to light. For, although in the former case the greater part of the reaction (54%) occurred by a Type I change, the hydrocarbon product was unsaturated, and consisted of an olefin of the composition C_6H_{12} [equation 4(*a*)], and not methyl*cyclo*pentane. Moreover, some 27% of the reaction could be represented by an alternative course, involving an internal splitting of the ring, as in equation 4(*b*).



. . (4)

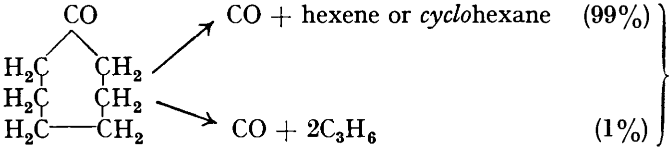
These results were sufficiently contrasted to the previous observations on *cyclo*hexanone to lead us to a further study of the reactions of these substituted cyclic ketones. It first appeared that the introduction of a methyl group into the ring would bring about a profound modification in the course of photochemical change, and results obtained with 2- and 4-methyl*cyclo*hexanones have partly substantiated this view. With 4-methyl*cyclo*hexanone a reaction corresponding to 4(*b*) occurs to an appreciable extent, and with all these compounds unsaturated hexenes were always formed by the Type I process, rather than methyl*cyclo*pentane, which would have been expected by analogy with the earlier work. The unexpected character of the results led us to repeat the earlier work on *cyclo*hexanone, with the result that a discrepancy came to light which we have not been able fully to resolve. For, although the relevant analytical data for *cyclo*hexanone in the present work check closely with those of the earlier, and although also it was confirmed that *cyclo*hexanone decomposes exclusively by a Type I mechanism, yet an unsaturated compound instead of the saturated *cyclo*paraffin resulted from the Type I decomposition. With suberone also the same discrepancy appeared. The main distinction between the olefin and the *cyclo*paraffin lies in their behaviour towards bromine water, and it is on this test that the above discrepancy mainly rests. The physical properties of the two types of compound are, however, also sufficiently distinct to make discrimination between them possible with accurate working. It appeared possible that the nature of the hydrocarbon might vary with wave-length or some other physical factor such as temperature, and that, for example, although *cyclo*paraffin may be formed when long wave-lengths (small energies) are used, yet the olefins may occur more readily with short wave-lengths. This we have not been able to substantiate owing to the difficulty of obtaining sufficiently strong monochromatic sources but the nature of the products appears to be independent of variation of temperature between 0° and 100°.

Until further and more refined experiments are possible, we reserve our judgment on the origin of this discrepancy, and merely express the view that, according to some physical factor as yet undetermined, the decomposition of *cyclo*hexanone and suberone is represented by the equations:



CO + pentene or *cyclo*pentane (87%)

$CO + C_2H_4 + C_3H_6$ (13%) . . . . (5)



CO + hexene or *cyclo*hexane (99%)

$CO + 2C_3H_6$ (1%) . . . . (6)

It may be noted in support of this view that Bawn and Hunter, who have recently isolated the trimethylene diradical (*Trans. Faraday Soc.*, 1938, **34**, 608), have shown it to isomerise in two ways, to give propylene and *cyclo*propane in comparable amounts. They also found that the ratio of the two isomers varied as the pressure of inert gas was changed. There can be little doubt that the penta- and the hexa-methylene diradicals are produced in our case, and it is not improbable that the extent of cyclisation varies with the energy of the photolysing quantum.

A comparison of the decompositions of these cyclic ketones brings to light the marked dependence of the type of photochemical reaction upon small changes of molecular structure. The results show clearly, however, that the photolysis can in every case be described in terms of Types I and II, together with the "intermediate" type previously noted for methyl ethyl ketone (see Bamford and Norrish, J., 1935, 1504). The last resembles Type I in that a carbonyl bond is broken, but differs in that the products are an olefin and an aldehyde. In the later discussion it will be termed Type III:

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_3 \longrightarrow CH_3{\cdot}CHO + C_2H_4 \quad . \; . \; . \; . \; . \quad (7)$$

It will appear from the discussion that the intervention of free radicals into the Type II photolysis of cyclic ketones is unlikely, just as it has previously been shown unlikely in the case of open-chain compounds.

EXPERIMENTAL.

The apparatus employed has been described previously (see, *e.g.*, Norrish and Appleyard, J., 1934, 874). It consisted essentially of a quartz vessel in which the compound being studied was refluxed in a vacuum by gentle heating, the vapour being exposed to the full light of the mercury arc. The liquid was protected from the light. The reaction vessel was in communication with a litre globe, wherein collected the greater part of the products, away from further light action. After irradiation, the products were divided into fractions according to their volatility, by cooling the reaction vessel to a suitable temperature, and distilling off any volatile substances in a vacuum. Cooling mixtures employed were liquid nitrogen (— 196°), mixtures of liquid nitrogen and alcohol (— 100° to — 120°), solid carbon dioxide and ether (— 78°), ice–hydrochloric acid (— 25°), ice at 0°, etc. Gaseous products were subsequently removed by a Toepler pump and analysed in a Bone and Wheeler apparatus.

Liquids were distilled into weighed tubes, which were then sealed and reweighed. They were identified by their physical properties (*e.g.*, f. p., b. p., vapour pressures, and vapour density) and chemical reactions. When possible, a crystalline derivative was prepared and its m. p. taken.

The menthone used was a specially purified specimen, kindly supplied by Professor Read of St. Andrew's University. The three methyl*cyclo*hexanones were purchased, and purified by fractionation. The b. p.'s were: 2-, 162°; 3-, 169°; 4-, 164° (760 mm.). *cyclo*Hexanone was obtained by purifying the commercial product by means of its bisulphite compound; b. p. 154°. *cyclo*Heptanone was prepared by the method of Mosettig and Burger (*J. Amer. Chem. Soc.*, 1930, **52**, 3456) and purified similarly; b. p. 180°.

l-*Menthone.*

The results of three experiments are given below. A specimen run is described fully in Table I, while Table II gives only total volumes of products, without further details of the analysis. In each case the temperature of the vapour was 80°.

TABLE I.

Volumes of products in c.c. of vapour at *N.T.P.*
Temp., 80°. Press., 2 mm. Irradiation for 95 hours.

Fraction.	Temp. of removal.	H_2.	CH_4.	C_2H_6.	CO.	C_3H_6.	$CH_3{\cdot}CHO$.	C_5H_8.	Methyl-*cyclo*-hexanone.	C_6H_{12}.
I	−190°	0·4	0·3	—	13·2	—	—	—	—	—
IIA	−110	—	—	0·2	—	20·1	—	—	—	—
IIB	−110	—	—	—	—	16·4	—	—	—	—
IIc	−100	—	—	—	—	1·7	3·3	—	—	—
III	− 78	—	—	—	—	—	2·8	6·4	—	—
IVA	0	—	—	—	—	—	—	—	6·0	12·8
IVB	0	—	—	—	—	—	—	—	10·0	—
IVc	0	—	—	—	—	—	—	—	1·5	—
	Totals	0·4	0·3	0·2	13·2	38·2	6·1	6·4	17·5	12·8

TABLE II.

Volumes of products in c.c. at *N.T.P.* Temperature 80°.

Expt.	Pressure of vapour, mm.	H_2.	CH_4.	C_2H_6.	CO.	C_3H_6.	$CH_3{\cdot}CHO$.	C_5H_8.	Methyl-*cyclo*-hexanone.	C_6H_{12}.
I	2	0·4	0·3	0·2	13·2	38·2	6·1	6·4	17·5	12·8
II	2	3·4	3·2	2·5	23·6	22·8	2·0	5·0	5·9	9·9
III	20	—	0·2	0·2	2·0	15·0	0·7	0·8	13·0	1·6

The fractions removed at temperatures below − 100° were analysed by the standard methods of gas analysis.

Fraction IIc (Table I), which was pumped off with the Toepler pump, contained a portion which was readily liquefied by compression in the gas burette. Pressure–volume measurements enabled the vapour pressure of this portion at room temperature to be estimated, and also the fraction of the whole which it constituted. The physical properties of the compound are shown below, and compared with those of acetaldehyde:

	Liquid from fraction IIc.	$CH_3{\cdot}CHO$.
V. p. at 18·5°	693 mm.	700 mm.
M	40	44
B. p.	21°	20·2°
F. p.	−120°	−121°

The liquid was completely miscible with water, and had the smell and all the reactions of acetaldehyde. It was therefore identified with the latter.

The permanent gas remaining in the gas burette was completely soluble in bromine water, and when mixed with oxygen and sparked, exploded as C_3H_6.

The fractions removed at − 78° were partly soluble in water. Each was treated in the following manner. The liquid was mixed with an equal volume of water, cooled to − 30°, and the upper (unfrozen) layer distilled off in a vacuum and weighed. A microcombustion and vapour-density determination showed that the distillate was an unsaturated hydrocarbon of formula C_5H_8, and this was in agreement with its chemical properties. The b. p. was sharp, and constant at 45° for the whole of the liquid, so it appeared improbable that the latter was a mixture of isomers. The only isomers which could reasonably be expected were α- and β-methylbutadiene. The latter was excluded because of its low b. p., 35°. The former compound boils at 44°, which is close to the b. p. of the hydrocarbon under examination. It was considered, therefore, that the liquid was α-methylbutadiene, and this conclusion is in complete agreement with the remainder of the analysis, as will appear later.

The aqueous portion remaining behind after removal of the hydrocarbon had the smell of acetaldehyde. It restored the colour to Schiff's reagent, responded to the iodoform test, gave a brown-grey precipitate with Nessler's solution, and reduced Fehling's solution. It was thus identified as a solution of acetaldehyde.

Fraction IVA had in each experiment a very indefinite b. p.: boiling commenced at 70° and continued until over 170°. By treatment with sodium bisulphite solution and subsequent distillation in a vacuum it was possible to remove a volatile portion. Microanalysis showed that this substance had the empirical formula CH_2, and a vapour density measurement gave 84 as the molecular weight, and consequently C_6H_{12} as the molecular formula. In each case the liquid boiled from 67° to 68°, and reacted readily with bromine water. This b. p. is that of β-methyl-Δ^{β}-pentene, and although the evidence is not sufficient to decide definitely between the various isomers of the formula C_6H_{12}, the physical properties indicate this to be the most probable.

The bisulphite compound obtained from fraction IVA was decomposed by warm 10% caustic potash solution, and the regenerated ketone distilled off in a vacuum and dried by calcium chloride. It was removed from the latter by distillation in a vacuum to a tube cooled in liquid air, and weighed. The major portion of the liquid boiled between 169° and 170°, and appeared to be identical with 3-methyl*cyclo*hexanone (b. p. 169°). The oxime melted between 41° and 44° in each experiment. That of 3-methyl*cyclo*hexanone melts at 43·5°.

Fractions IVB and IVC were similarly treated with sodium bisulphite solution and thus shown to consist mainly of 3-methyl*cyclo*hexanone, together with a little menthone. The latter does not form a bisulphite compound; this property was made use of in separating it from the methyl*cyclo*hexanone.

These results, coupled with those described below for 3-methyl*cyclo*hexanone, show that the course of photolysis is correctly represented by equations 3, 4(*a*), (*b*), and (*c*). According to these equations the following relations should hold between the volumes of the products:

(1) $[C_5H_8] = [CH_3{\cdot}CHO] + [CH_4]$
(2) Total saturated hydrocarbons + $[C_6H_{12}] = [CO]$
(3) Methyl*cyclo*hexanone + $[CH_3{\cdot}CHO] + [CH_4] + [C_6H_{12}] = [C_3H_6]$

The table below shows that the experimental results are in agreement with these deductions.

Expt.	$[C_5H_8]$.	$[CH_3{\cdot}CHO]$ + $[CH_4]$.	Total satd. hydrocarbons + $[C_6H_{12}]$.	[CO].	Methyl*cyclo*hexanone + $[CH_3{\cdot}CHO]$ + $[CH_4]$ + $[C_6H_{12}]$.	$[C_3H_6]$.
I	6·4	6·4	13·7	13·2	36·7	38·2
II	5·0	5·2	19·0	23·6	21·0	22·8
III	0·8	0·9	2·0	2·0	15·3	15·0

It is to be noted that no hydrocarbon of the formula C_9H_{18}, which would be produced by a decomposition according to Type I, was found; moreover, it could not have been formed in appreciable quantities, since the equality expressed in (2) above is found to hold.

3-*Methyl*cyclo*hexanone.*

The results obtained are shown below:

Volumes of products in c.c. of vapour at *N.T.P.*
Pressure, 5 mm. Irradiation for 100 hours with full arc.

Fraction.	Temp. of removal.	CO.	H_2.	CH_4.	C_2H_4.	$CH_3{\cdot}CHO$.	C_5H_8.	C_6H_{12}.
I	−190°	20·2	0·1	0·2	—	—	—	—
II	− 95	—	—	—	1·4	0·7	—	—
III	− 78	—	—	—	—	6·6	—	—
IV	− 25	—	—	—	—	—	7·8	—
V	− 0	—	—	—	—	—	—	15·0
	Totals	20·2	0·1	0·2	1·4	7·3	7·8	15·0

Fraction I was analysed in the ordinary way. Fraction II contained a portion soluble in water, and the solution had the smell and reactions of acetaldehyde; the residual gas analysed as ethylene. Fraction III consisted of a volatile liquid, with physical properties very similar to those of acetaldehyde. The heats of evaporation (calculated from the determined vapour-pressure curve) and the b. p. and f. p. of the liquid and of acetaldehyde are given below:

	Fraction III.	Acetaldehyde.
Heat of evaporation, kg.-cals./mol.	6·63	6·62
B. p.	22°	20·2°
F. p.	−125°	−121°

The substance also possessed all the reactions of acetaldehyde: in particular it was oxidised by hydrogen peroxide to acetic acid, which was identified, after removal of excess peroxide with silver oxide, by the production of ethyl acetate on warming with ethyl alcohol and sulphuric acid.

A micro-combustion performed on fraction IV gave C_5H_8 as the formula for the compound, and a vapour-density determination gave *M*, 67 (Calc.: *M*, 68). This substance boiled at 45° and exhibited typical unsaturation reactions with bromine water and alkaline potassium permanganate. It appeared to be identical with the hydrocarbons found in fraction III in the menthone experiments, and for reasons similar to those given previously it was considered to be α-methylbutadiene. Fraction V was treated exactly as described for fraction IVA on p. 1525, and thus identified as a hexene, probably β-methyl-Δ^{β}-pentene.

These results show that the photodecomposition of 3-methyl*cyclo*hexanone follows the course of equations 4(*a*), (*b*), (*c*). The photolysis of a small quantity of acetaldehyde accounts for the presence of the methane found. The volume relations between the products which follow from these equations are borne out satisfactorily by the experimental results. They are:

(i) $$[C_6H_{12}] + [CH_4] + \tfrac{1}{3}[C_2H_4] = [CO]$$

Experimentally, the left-hand side of this equation was found to be 15·7 c.c., whereas 20·2 c.c. of carbon monoxide were obtained.

(ii) $$[CH_3{\cdot}CHO] + [CH_4] = [C_5H_8]$$

The experiment shows that the volume of acetaldehyde and methane together was 7·5 c.c. This is close to the volume of α-methylbutadiene produced, *viz.*, 7·8 c.c.

4-*Methyl*cyclo*hexanone.*

The volumes of the products obtained in an experiment on the photodecomposition of 4-methyl*cyclo*hexanone vapour are given below in c.c. at *N.T.P.*

Press., 5 mm. Temp., 80°. Irradiation for 100 hours, with full arc.

Fraction.	Temp. of removal.	H_2.	CH_4.	CO.	C_2H_4.	$CH_3{\cdot}CHO$.	C_5H_8.	C_6H_{12}.
I	−190°	0·7	0·25	33·2	—	—	—	—
II	−110	—	—	—	1·8	—	—	—
III	− 80	—	—	—	—	10·2	5·0	—
IV	− 80	—	—	—	—	4·6	5·9	—
V	− 30	—	—	—	—	—	2·3	5·6
VI	− 10	—	—	—	—	—	—	22·2
VIA	− 10	—	—	—	—	—	—	5·6
	Totals	0·7	0·25	33·2	1·8	14·8	13·2	33·4

The analyses of fractions I and II call for no special comment. Fractions III and IV contained portions which were soluble in water. They were each treated in the manner described previously for the third fraction in the photolysis of menthone. The more volatile portion, insoluble in water, analysed in each case as C_5H_8, and vapour-density determinations gave this as the molecular formula. The vapour-density results and b. p.'s are given below:

	Hydrocarbons from Fraction III.	Hydrocarbons from Fraction IV.
B. p.	35°	35·5°
M	67	67·5

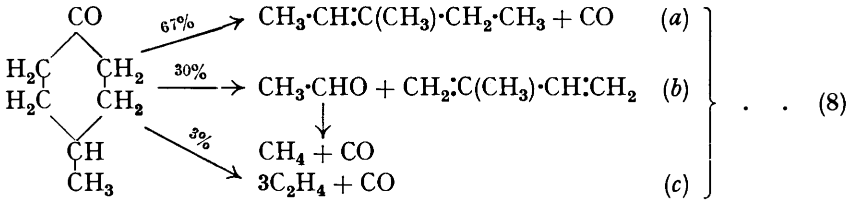
The liquids exhibited unsaturation reactions with bromine water and alkaline permanganate. The b. p.'s lie very close to that of isoprene, 35°, and it was considered that the liquids consisted of this compound, for this is the only hydrocarbon of formula C_5H_8 which may be reasonably expected to result from decomposition of 4-methyl*cyclo*hexanone, and its presence in fractions III and IV is entirely in agreement with the rest of the analysis.

The aqueous portions remaining after the removal of the hydrocarbons had the smell and properties of acetaldehyde: the liquids restored the colour to Schiff's reagent, responded to the iodoform test, and gave a brown-grey precipitate with Nessler's solution. Oxidation with hydrogen peroxide, as described above, produced acetic acid, identified as before. Colorimetric estimations, using Schiff's reagent, gave the weights of acetaldehyde present, agreeing to within 3% with those obtained by direct weighing, the hydrocarbon being weighed after removal, and the aldehyde estimated by difference.

Fraction V was shown to be a mixture of substances, since its vapour pressure fell steadily on fractionation in a vacuum at constant temperature. A microanalysis showed that carbon and hydrogen only were present. In view of the fact that the following fractions consisted of a hydrocarbon C_6H_{12}, it was considered that the liquid was composed of a mixture of C_6H_{12} with C_5H_8, the latter being incompletely removed in Fraction IV. The presence of ethylene or other low hydrocarbons was unlikely, since these substances did not appear in Fraction IV. A vapour-density determination gave *M*, 80, and this enabled the proportions of C_5H_8 and C_6H_{12} to be calculated. The mixture boiled over the range 40—80°; the b. p.'s of the constituents are 35° and 68° respectively. The liquid reacted rapidly and completely with bromine water.

Fractions VI and VIA had a smell characteristic of unsaturated hydrocarbons, and a faint trace of 4-methyl*cyclo*hexanone was present also. The latter was removed by treatment with sodium bisulphite solution and distillation, in the manner described previously. The distillates analysed as CH_2, and in each case the molecular weight, determined by measurements of the vapour density, was found to be 84. The hydrocarbon was thus C_6H_{12}; it gave the usual unsaturation reactions. The liquids boiled between 67° and 70°, and hence probably consisted of γ-methyl-Δ^{β}-pentene, b. p. 69·5—71°. The scanty data available for these compounds make it difficult to decide definitely whether this was the isomer actually formed; the physical properties indicate that it is the most probable.

The results are in agreement with the following scheme for the photolysis of 4-methyl*cyclo*hexanone vapour.



This scheme predicts the following volume relations between the products:

(1) $[CO] - [CH_4] - \frac{1}{3}[C_2H_4] = [C_6H_{12}]$

Experimentally, $[CO] - [CH_4] - \frac{1}{3}[C_2H_4] = 32{\cdot}3$ c.c., and $[C_6H_{12}] = 33{\cdot}4$ c.c.

(2) $[CH_3{\cdot}CHO] + [CH_4] = [C_5H_8]$

Experimentally, $[CH_3{\cdot}CHO] + [CH_4] = 15{\cdot}1$ c.c., and $[C_5H_8] = 13{\cdot}2$ c.c.

The quantitative results thus confirm the above mechanism.

2-*Methyl*cyclo*hexanone.*

The results obtained in two experiments with this compound are given below. Experiment (1) is given in detail, experiment (2) in summary. Volumes are given in c.c. of vapour at *N.T.P.*

Press., 5 mm. Temp., 80°. Irradiation for 50 hours with full arc.

Fraction.	Temp. of removal.	CO.	CH_4.	C_2H_4.	C_5H_{10}.	C_6H_{12}.	*cyclo*Hexanone.
I	−190°	66·1	3·2	—	—	—	—
II	−110	—	—	5·0	—	—	—
III	− 80	—	—	—	5·0	4·7	—
IV	− 30	—	—	—	—	56·1	—
V	0	—	—	—	—	—	10·1
	Total, Expt. (1)	66·1	3·2	5·0	5·0	60·8	10·1
	Total, Expt. (2)	100·2	0·26	11·5	10·7	89·5	12·1

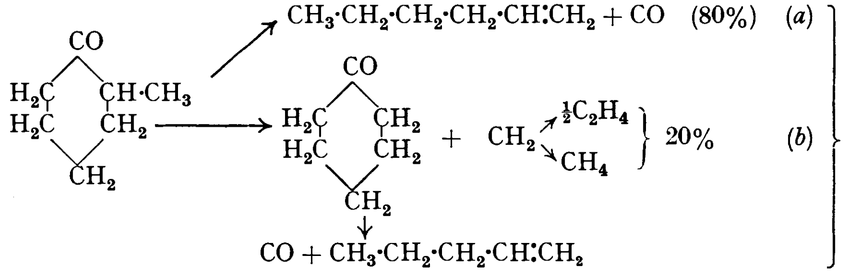
Little comment is needed in connection with the analyses given above. It is interesting that no aldehyde could be detected in any of the fractions. Fraction III in both experiments consisted of a volatile liquid whose vapour pressure fell as successive portions were distilled off in a vacuum. The liquids therefore contained two or more substances, and in each case the following procedure was adopted. The liquid was cooled to — 50°, and the vapour was passed through a spiral at the same temperature and condensed in liquid air. It was thus possible to distil off a portion which appeared to be a single compound. In both experiments this compound micro-analysed as CH_2 and the vapour density gave M, 69·5. The molecular formula was therefore, C_5H_{10}. The liquids boiled over the range 39—40°. These properties identify the substances as α-amylene, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, b. p. 39°. The vapour density measurements were made with a maximum error of 1%; these, and the b. p.'s given above, show definitely that the hydrocarbon being examined was C_5H_{10} and not C_5H_8, as found in the preceding decompositions of menthone and 3- and 4-methyl*cyclo*hexanone.

The less volatile portion of fraction III also analysed as CH_2 in each case. Vapour-pressure measurements showed that the liquids were mixtures, however, and molecular weights between those of C_5H_{10} and C_6H_{12} were determined. Since the latter hydrocarbon is the sole constituent of fraction IV it is justifiable to conclude that the less volatile portion of fraction III was a mixture of C_5H_{10} and C_6H_{12}. The proportions of each present were calculated from the molecular weights. Fraction III reacted readily with bromine water.

Fraction IV in each case was a hydrocarbon which analysed as CH_2, and had a molecular weight of 83·5. Its formula was, therefore, C_6H_{12}. It reacted completely with bromine water and therefore was not a cyclic hydrocarbon. Its b. p. was 66°. These properties justify its identification with α-hexene, b. p. 67°.

The fractions removed at 0° were treated with an excess of sodium bisulphite solution. A considerable quantity of solid bisulphite compound was produced in each case. The unchanged 2-methyl*cyclo*hexanone was distilled off in a vacuum. (This ketone, like menthone, does not form a bisulphite compound, presumably for reasons of steric hindrance.) On treating the solids with a little caustic potash solution an oil was formed, which had the smell of *cyclo*hexanone. The whole of the liquid was distilled off, and the water removed by calcium chloride in a " vacuum desiccator," which consisted of an inverted U-tube, with the calcium chloride in one limb, and the liquid to be dried in the other. The liquids finally obtained were identical with *cyclo*hexanone. The b. p. in each case was 156° and the oximes melted at 86·5°. The corresponding figures for *cyclo*hexanone are 156° and 88°.

The main process in the photodecomposition of 2-methyl*cyclo*hexanone is thus a decomposition into α-hexene and carbon monoxide. The production of *cyclo*hexanone, however, shows that a Type II decomposition also occurs; the complete scheme is shown below:



(9)

The small quantities of methane formed are considered to arise from the hydrogenation of CH_2 radicals.

This scheme predicts the following relation between the volumes of the products:

(1) $[CO] = [C_6H_{12}] + [C_5H_{10}]$
(2) $2[C_2H_4] + [CH_4] =$ *cyclo*hexanone $+ [C_5H_{10}]$

The experimental figures given in the table below are in satisfactory agreement with these equations.

Expt.	[CO].	$[C_6H_{12}] + [C_5H_{10}]$.	$2[C_2H_4] + [CH_4]$.	*cyclo*Hexanone $+ [C_5H_{10}]$.
I	66·1	65·8	13·2	15·1
II	100·2	100·2	23·3	22·8

Equations 9 (*a*) and (*b*) also predict that in a number of experiments $[C_6H_{12}]/V$ should be constant, where V is equal to the sum of the volumes of *cyclo*hexanone vapour and C_5H_{10}. This is the case experimentally; the ratio has the values 4·0, 3·8 in Expts. I and II respectively.

Thus the quantitative results leave little doubt that equation (9) represents the correct mechanism of photolysis.

cyclo*Hexanone.*

The following results were obtained. Volumes of products are given in c.c. at *N.T.P.*

Press., 5 mm. Temp., 80°. Irradiation for 20 hours with full arc.

Fraction.	Temp. of removal.	H_2.	CH_4.	CO.	C_2H_4.	C_3H_6.	C_5H_{10}.
I	−190°	0·7	1·0	58·4	—	—	—
II	−110	—	—	—	1·2	0·8	—
III	− 80	—	—	—	1·5	1·9	5·4
IV	0	—	—	—	—	—	45·3
	Totals	0·7	1·0	58·4	2·7	2·7	50·7

The first two fractions were analysed by standard methods of gas analysis.

Fraction III was a volatile liquid, which microanalysed as CH_2. Vapour-pressure mea ments on portions of it showed that it was a mixture, which contained some substance an appreciable vapour pressure at — 90°. The whole of the liquid dissolved readily in bromine water. Since fraction IV consisted mainly of C_5H_{10} (α-amylene), it was considered that the mixture contained C_5H_{10}, ethylene, and propylene, as the last two compounds had been identified in fraction II. Observations on the b. p. of the liquid agreed with this idea; most of the substance boiled between 38° and 39°, but a more volatile portion with no definite b. p. was also present (b. p. of α-amylene, 39°). The mixture was analysed by explosion with excess oxygen. For this purpose oxygen was added to a small weighed quantity of the liquid in a gas burette, care being taken to ensure that the whole of the liquid was vapourised, and that only unsaturated vapour was present. The mixture was then passed into the explosion pipette and sparked. The explosion results gave as the composition of fraction III : C_2H_4, 1·5; C_3H_6, 2·0; C_5H_{10}, 5·3 c.c. These figures were supported by vapour-density measurements. The vapour density calculated for a mixture of the above composition is 56·5, that actually observed was 56·0. In order to confirm the presence of ethylene and propylene, a careful fractionation was performed. The most volatile portion was drawn off from the mixture cooled to — 80°, passed through a glass spiral in a freezing mixture at — 100°, and finally condensed in a small liquid-air trap. This consisted of permanent gas; no condensation occurred on increasing the pressure in the gas burette to 2 atm. The gas when sparked with oxygen exploded as a mixture of approximately equivalent volumes of ethylene and propylene. These experiments justify the opinion that fraction III had the composition expressed above.

Fraction IV was also a volatile liquid of empirical formula CH_2. A vapour-density determination gave *M*, 71·5. Observations of the vapour pressure suggested that it was a single compound, and this was confirmed by the fact that the b. p. was sharp, 38—39°. The molecular formula was, therefore, C_5H_{10}. The f. p. was difficult to determine, but the liquid set to a jelly between — 140° and — 145°. These physical properties are quite different from those of *cyclo*pentane, the b. p. and f. p. of which are respectively 49·5° and — 93·3°. Further, it was found that fraction IV, both in the gas and in the liquid phase, was readily reactive to bromine water. On treating it with excess bromine water, and distilling off volatile products in a vacuum at 0°, the dibromide (b. p. 191°) was obtained in 88% yield. It was concluded that the liquid was mainly α-amylene (b. p. 39°, f. p. *ca.* — 135°).

The results show that the decomposition is correctly represented by equation (5) (p. 1523). The figures given above show that propylene and ethylene are produced in equivalent quantities (2·7 c.c.) in accordance with this scheme, and moreover, that the volume of carbon monoxide (58·4 c.c.) is approximately equal to the sum of the volumes of ethylene and amylene (53·4 c.c.).

The experiment was repeated with the vapour maintained at a constant temperature by a water-bath. Temperatures of 40° and 80° were used. In a fourth run the decomposition was carried out in the presence of 0·5 atm. of carbon dioxide, in an attempt to stabilise any *cyclo*pentane which may have been formed. In all cases only the olefin could be identified; there appeared to be no formation of *cyclo*paraffin. By passing the vapour of the latter through a quartz tube heated in an electric furnace, it was shown that below about 600° little or no isomerisation into the olefin occurs. Above 600° decomposition into lower hydrocarbons takes place. Thus the results cannot be accounted for by isomerisation of *cyclo*paraffin formed in the primary act.

cyclo*Heptanone*.

The volumes of products (c.c. of vapour at *N.T.P.*) of photolysis are given in Table III.

TABLE III.

Press., 4 mm. Temp., 80°. Irradiation for 30 hours with full arc.

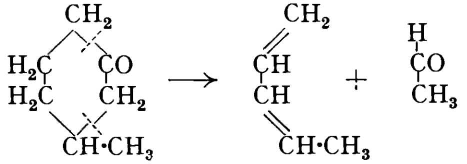
Fraction.	Temp. of removal.	CH_4.	H_2.	CO.	C_3H_6.	C_6H_{12}.
I	−190°	1·4	0·5	36·2	—	—
II	−110	—	—	—	1·0	—
III	− 80	—	—	—	—	35·2
IV	0	—	—	—	—	
	Totals	1·4	0·5	36·2	1·0	35·2

The only portion of the analysis which needs consideration here is the examination of fractions III and IV. These appeared to consist of the same substance; in each case the liquid had the empirical formula CH_2, and a vapour density of 83·5. Both liquids were single substances, as shown by the constancy of the vapour pressures during fractionation in a vacuum, and by the sharp b. p.'s, 67—68°. The compounds readily reacted with bromine water, and behaved with alkaline permanganate in a manner typical of an olefin. It was considered, therefore, that fractions III and IV consisted of α-hexene, b. p. 67°. This was confirmed by the direct formation of dibromohexane (b. p. 99°/15 mm.) in 90% yield by treatment with excess bromine water, and removal of the volatile residue in a vacuum at 0°.

Thus the decomposition is that represented by equation (6). An inspection of Table III shows that the carbon monoxide (36·2 c.c.) was approximately equivalent to half the propylene, together with the hexane (35·7 c.c.), as predicted by (6).

DISCUSSION.

The photolysis of menthone vapour occurs almost exclusively according to Type II, although the subsequent decomposition of the resulting 3-methyl*cyclo*hexanone yields a number of secondary products. This splitting off of the *iso*propyl group is one of the best examples of this type of decomposition, and strengthens the contention previously adduced that the process is one which does not involve free radicals. In the case of all Type II decompositions, the reaction is most simply visualised as a molecular rearrangement. It seems clear that when the side chain is suitably placed with respect to the carbonyl group this type of decomposition is strongly favoured. This is not the case for the 3- and 4-methyl*cyclo*hexanones, and consequently the products are more complex. Decomposition occurs mainly by Type I, the splitting out of carbon monoxide from the ketone molecule leaving an open-chain diradical, which readily changes into the isomeric unsaturated hydrocarbon. To a small extent in each case these radicals also break into simpler smaller radicals, which yield ethylene. These two modifications of Type I account for some 70% of the total decomposition. The remainder occurs by a process which involves a double break in the molecule, with formation of an aldehyde, by a process which is formally a combination of Types II and III (see p. 1523):



Type III reaction appears to be of restricted occurrence, having only been observed previously to a very small extent with methyl ethyl ketone. In the case of 2-methyl*cyclo*hexanone a true Type II reaction, with splitting off of a methylene group from the molecule, becomes possible, and in agreement with the above views *cyclo*hexanone itself was detected in considerable quantity among the decomposition products, while there was also a corresponding yield of ethylene and methane. With *cyclo*hexanone and suberone decomposition is according to Type I, and similar, but decomposition by Types II or III is completely absent. The products show that after elimination of carbon monoxide there is produced a straight-chain diradical which, as in the previous cases, isomerises to the olefin containing the same number of carbon atoms per molecule. A small proportion of the radicals break down to ethylene and propylene (*cyclo*hexanone) or to propylene (suberone). Analytically, the above results are identical with the observations previously published on these substances (Saltmarsh and Norrish, J., 1935, 1504), but the earlier identification of the main hydrocarbon products as *cyclo*paraffin leaves a discrepancy which has not yet been resolved. By analogy with the work of Bawn and Hunter on the trimethylene diradical, there may be some special condition favourable to the formation of *cyclo*paraffins which has not been reproduced.

The general conclusion which can be drawn from the above results is that cyclic ketones behave similarly to other aliphatic ketones, and that where possible (*i.e.*, when there is a side chain suitably placed), decomposition of Type II occurs very readily. In the absence of this possibility, decomposition according to Type I with production of olefins predominates. With the methyl-substituted compounds a more restricted third type has been observed.

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