191. *Primary Photochemical Reactions. Part IV. Decomposition of Methyl Ethyl Ketone and Methyl Butyl Ketone.*

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THE photochemical decomposition of many aldehydes in the gaseous state is now known to take place by the simple reaction $R \cdot CHO = RH + CO$ to the extent of at least 95% (Norrish and Kirkbride, J., 1932, 1518). Since the hydrocarbon RH is formed in such

predominantly large proportion, it has been suggested (*idem, ibid.*) that each molecule of hydrocarbon has its origin from a single molecule of aldehyde, and that the process does not take place by the scission of free radicals or hydrogen atoms, for if this were the case, appreciable quantities of hydrogen and the hydrocarbon R·R would be expected, whereas the yield of hydrogen is rarely more than about 2% of the total gaseous products.

In order to obtain further insight into the mechanism involved, it is desirable to find whether the analogous decomposition of the vapours of ketones is equally simple. Acetone vapour gives mainly carbon monoxide and ethane in nearly equivalent proportions (Berthelot and Gaudechon, *Compt. rend.*, 1910, **151**, 478; 1912, **155**, 207; see also Part V of this series). It is not clear, however, whether decomposition occurs by way of free radicals, or whether each molecule of ethane has its origin in a single molecule of acetone.

To distinguish as far as possible between these possibilities we have now studied the photochemical decomposition of the two mixed ketones named in the title. The results show clearly that the simple change $COR_1R_2 \longrightarrow R_1 \cdot R_2 + CO$ does not take place, for methyl ethyl ketone yields the three hydrocarbons, ethane, propane, and butane, in nearly equal quantities, together with an equivalent of carbon monoxide.

If it be argued, in spite of these results, that the paraffin is really produced initially as pure propane of such high energy content that the molecules react among themselves to give ethane and butane, we may cite the analogous decomposition of *iso*butaldehyde where propane is produced almost exclusively (Franke and Pollitzer, *Sitzungsber. K. Akad. Wiss. Wien*, 1913, **122**, 2B, 183; *Monatsh.*, 1913, **34**, 797); if there were any instability about the freshly formed molecules of hydrocarbon, we should expect a mixture in each case instead of only in one.

The primary decomposition of methyl butyl ketone almost quantitatively follows the unexpected course

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3 \longrightarrow CH_3 \cdot CH{:}CH_2 + CH_3 \cdot CO \cdot CH_3 \quad . \quad . \quad (1)$$
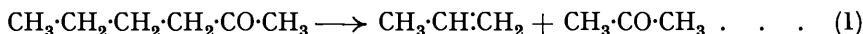
and the production of small quantities of ethylene in the decomposition of methyl ethyl ketone suggests that this also undergoes a similar primary change to a limited extent :

$$C_2H_5 \cdot CO \cdot CH_3 \longrightarrow CH_2{:}CH_2 + CH_3 \cdot CHO \quad . \quad . \quad . \quad (2)$$
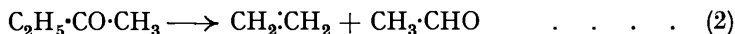
These results raise certain questions relative to the transfer of energy from the chromophoric group to other parts of the molecule which are of fundamental importance; they are discussed on p. 878.

Both the ketones now studied, like acetone, have the absorption band characteristic of the carbonyl group, extending from about 3300 to 2200 Å.U. Absorption of light in this region leads to the photochemical decomposition mentioned above. The spectroscopic evidence and fluorescence data of other carbonyl substances, particularly of formaldehyde and acetone, show that the decomposition is a spontaneous disruption, for the absorption spectra show the characteristics of predissociation, especially with reference to fluorescence. These data will be discussed in a paper (Part V) on the decomposition of acetone vapour, in which the whole of the evidence is critically examined.

<div align="center">EXPERIMENTAL.</div>

Methyl ethyl ketone was obtained from Messrs. Hopkin and Williams; methyl butyl ketone was prepared from ethyl acetoacetate and propyl iodide. Both ketones were purified through their sodium bisulphite compounds, followed by repeated fractional distillation; b. p.'s 79·5° and 127° respectively.

The apparatus used for the photochemical decomposition is shown in the fig. The quartz flask *A* had a neck 8 cm. long and 2 cm. wide and was attached by way of a ground-glass stopper to the double-surface water-condenser *B* and the litre globe *C*. The whole apparatus could be evacuated by way of *D* through a Toepler pump. By completely evacuating and then cooling *A* in liquid air, about 5 g. of ketone were distilled into *A* from a side reservoir *F*. The tap *D* was then closed, and the liquid air removed from *A*, the ketone being allowed to reflux under gentle heat from a small flame. The vapour in the neck of the flask was illuminated by a vertical

mercury lamp E, consuming 5 amps. at a terminal voltage of 150. The products of photodecomposition gradually accumulated mainly in the large bulb C. After the illumination had

continued for a suitable time (specified below), the products of decomposition were removed by the Toepler pump and collected in three or more fractions. The first fraction was pumped off through a trap H cooled in liquid nitrogen, the quartz flask being similarly cooled, and consisted mainly of carbon monoxide, and also any methane or hydrogen if present. After the first fraction had been collected, the condensate in the trap was allowed to warm, and distilled back into the quartz flask. The second fraction was then pumped off, the trap and quartz flask being now cooled at some higher temperature. The process was repeated with the third and later fractions, progressively higher temperatures being used. The various fractions were separately analysed by standard methods.
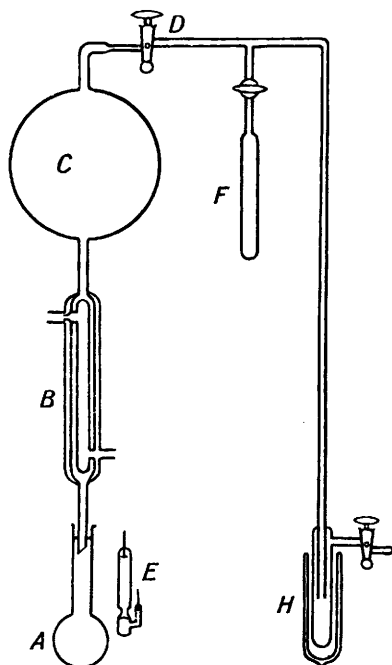
Methyl Ethyl Ketone.—On interposing a plate of " Vita " glass between the lamp and the reaction flask, scarcely any decomposition occurred; this showed that light of shorter wave-length than 3100 Å.U. was responsible for the photochemical change. Exposures were then made using the full light of the mercury lamp.

Experiment 1.—Exposure 12 hours. One portion of Fraction B after absorption of the olefin exploded accurately as ethane, and a second portion exploded as a whole as a mixture of ethylene and ethane.

Fraction.	Temp. at which it was pumped off.	Volume at 0°, c.c.							
		Total.	CO_2.	O_2.	CO.	CH_4.	C_2H_4.	C_2H_6.	Mixed paraffins exploding to C_3H_8.
A	− 196°	30·9	0	0	27·6	3·3	0	0	0
B	− 78 (1st fraction)	10·9	0	0	0	0	2·9	8·0	0
C	− 78 (2nd fraction)	19·0	0	0	0	0	2·6	0	16·4

Fraction C after removal of the olefin yielded a paraffin, part of which exploded as propane. That it was by no means pure propane, however, was shown by the fact that when a specimen was condensed in carbon dioxide–ether, and then allowed to warm, it exhibited the properties of a mixture of ethane, propane, and butane. This observation was carried out by introducing about 3 c.c. of the gas into a gas burette attached to a small, and completely evacuated tube of about 1 c.c. capacity. On cooling the tip of this tube in the freezing mixture nearly all the gas was liquefied. By adding ether, the cooling mixture was caused to warm by small stages. At − 60°, about 2 c.c. of the gas were liquefied, and the remainder appeared to behave as a perfect gas. The liquid persisted without perceptible change to − 45°, and between this temperature and − 35° about 1·1 c.c. of gas boiled off. The remainder was still liquid at − 28° and remained so in ice–hydrochloric acid at − 20°. The liquid boiled finally to about 0·8 c.c. of gas at some temperature above − 20° and below that of the room. The fraction of b. p. − 45° to − 35° was propane (b. p. − 44°), and the final fraction butane (b. p. − 0·5°). As far as could be judged, there was slightly more propane than butane.

Experiment 2.—Exposure 2½ hours. By separating the gaseous products into four fractions, as indicated, it was possible to make a partial separation of the hydrocarbons; for instance,

Fraction.	Temp. at which it was pumped off.	Volume, c.c. at 0°.								
		Total.	CO_2.	O_2.	CO.	CH_4.	C_2H_4.	C_2H_6.	C_3H_8.	C_4H_{10}.
A	− 196°	27·8	0	0	26·2	1·6	0	0	0	0
B	− 110	7·65	0·3	0	0	0	3·3	4·05	0	0
C	− 90	7·2	0	0	0	0	2·5	1·1	3·6	0
D	− 78	9·75	0	0	0	0	0·65	0	2·5	6·6

after removal of the olefin, fraction C exploded mainly as propane, and fraction D mainly as butane. Assuming C to be a mixture of ethane and propane, and D to be a mixture of propane

and butane, it was possible to calculate the quantities of these hydrocarbons present from the data of the explosion.

The percentage composition of the gaseous products is shown below; the results of a third but incomplete experiment are also shown.

Composition of gaseous products, %.

	CO.	CH$_4$.	C$_2$H$_4$.	C$_2$H$_6$.	C$_3$H$_8$.	C$_4$H$_{10}$.	CO$_2$.
Expt. 1	45·5	5·4	9·05	13·2	27		0
,, 2	50·0	3·05	12·3	9·8	11·6	12·5	0·55
,, 3	51·0	4·3	4·9	39·8			

From these results, it will be seen that 35—40% of the gaseous products consists of a mixture of ethane, propane, and butane in comparable proportions. This means that 70—80% of the reaction takes the course $CH_3 \cdot CO \cdot C_2H_5 \longrightarrow \frac{1}{3}(C_2H_6 + C_3H_8 + C_4H_{10}) + CO$; 20—25% of the reaction, as judged from the amount of ethylene produced, may take the course (2) (p. 875). The methane produced may in part originate from the secondary photodecomposition of the acetaldehyde: $CH_3 \cdot CHO \longrightarrow CH_4 + CO$. The main decomposition, yielding paraffin and carbon monoxide, thus gives a mixture of paraffins rather than a single substance, and the paraffin molecules cannot originate from a single molecule of ketone.

Methyl Butyl Ketone.—The gaseous products were here divided into three fractions: (1) by pumping off from liquid nitrogen through a trap cooled in liquid nitrogen, thus allowing any carbon monoxide, methane, or hydrogen to be separated; (2) by pumping off with the flask cooled to $-78°$ with solid carbon dioxide–ether, the trap being cooled at $-110°$; and (3), as for (2), but with the trap cooled in liquid nitrogen. The results are in Table I.

TABLE I.

Fraction.	Temp. at which it was pumped off.	Total.	CO$_2$.	O$_2$.	CO.	H$_2$.	CH$_4$.	C$_2$H$_6$.	C$_3$H$_6$.	Acetone.
					Volume, c.c. at 0°.					
		Experiment 1. Irradiated 4 hours.								
A	$-196°$	12·1	0	0	9·65	0·75	1·7	0	0	0
B	-110	72·5	0	0	0	0	0	4·3	68·2	0
C	-78	0	0	0	0	0	0	0	0	67·6
		Experiment 2. Irradiated 6½ hours.								
A	-196	20·4	0	0	17·4	1·9	1·2	0	0	0
B	-110	95·5	0	0	0	0	0	12·0	83·5	0
		Experiment 3. Irradiated 7 hours.								
A	-196	15·8	0	0	13·5	1·1	1·2	0	0	0
B	-110	54·8	0	0	0	0	0	9·9	44·7	0

Experiment 1.—In this case the larger fraction came off at $-110°$ and consisted predominantly of propylene as was shown by combustion of specimens, (1) after and (2) without absorbing the olefin. After all the gas had been pumped off, the trap was cooled in liquid nitrogen, and the flask in carbon dioxide–ether, a considerable liquid fraction C being slowly distilled into the trap. A small weighed tube with a constriction for sealing off was attached by pressure tubing to the section of the apparatus carrying the manometer. After complete evacuation, the liquid was distilled into this tube, and its vapour pressure measured at room temperature (16·5°) and found to be 154·5 mm. The liquid was then condensed back into the small tube by means of liquid nitrogen, and the tube sealed off and weighed. It was found that 0·175 g. of liquid had been collected.

With part of the liquid a microdetermination of b. p. showed that two-thirds boiled between 57° and 59° and the rest below 61°. By using mixtures of liquid nitrogen and alcohol, the remaining portion of the liquid was found to freeze sharply at $-94·5°$. These physical constants characterise the liquid as pure acetone (v. p. at 16·5°, 158 mm.; b. p. 56·5°; f. p. $-95°$). Since the boiling point appeared a little high, a similar microdetermination was made with pure acetone, which was found to have b. p. 57—58·5° by this method. Finally, it was found that the liquid fraction C showed all the qualitative reactions of a ketonic substance.

Experiment 2.—In the expectation that the ethane arises mainly from the secondary decomposition of acetone, the acetone produced in this run was distilled back into the undecom-

posed methyl butyl ketone in the reaction flask, and re-illuminated (Expt. 3). An increase in the proportion of carbon monoxide and ethane (see below) confirmed this hypothesis.

The percentage compositions of the gaseous products calculated from the results of Expts. 1, 2, and 3, were as follows :

Composition of gaseous products, %.

	CO.	H_2.	CH_4.	C_3H_6.	C_2H_6.
Expt. 1	11·4	2·0	0·95	80·6	5·1
„ 2	15·0	1·6	1·05	73·7	10·3
„ 3	19·2	1·6	·1·7	63·5	14·1

These results show that methyl butyl ketone decomposes primarily almost completely into an equimolecular mixture of propylene and acetone.
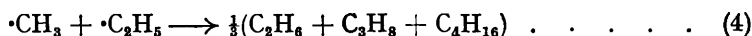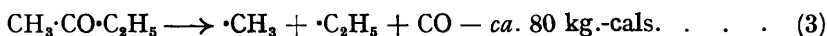
In Expt. 1 (Table I) the acetone formed is almost exactly equivalent to the propylene produced. The relationship of Expt. 3 to Expt. 2 described above shows that the ethane and part of the carbon monoxide result from the photodecomposition of the acetone.

DISCUSSION.*

The unexpected nature of the decomposition products of the two ketones raises certain considerations of fundamental interest. By comparison with the closely analogous case of acetone, it may be accepted that we have to deal in each case with a spontaneous unimolecular decomposition. The diffuseness of the absorption spectra of these ketones, though not in itself a completely reliable criterion of spontaneous decomposition, nevertheless becomes such when coupled with fluorescence data. With acetone vapour there is a sharp threshold of fluorescence near the beginning of the absorption spectrum, and in the region of diffuseness beyond 3000 Å.U. there is no trace of fluorescence even at low pressure. The spectroscopic interpretation of these facts will be discussed in the next paper, but in brief they may be taken as indicating that the molecule upon absorbing its quantum of active light passes to an upper level which is unstable and dissociates.

As has already been pointed out by one of us (Norrish, *Trans. Faraday Soc.*, 1934, **30**, 103), in dealing with the primary photochemical decomposition of molecules of this sort, however, there is an added complexity not found in simpler di- and tri-atomic molecules. For, whereas in these simpler cases, *e.g.*, chlorine or nitrogen peroxide, the link which is ruptured is also that which is concerned with light absorption, this cannot always be said to be the case when the molecule contains a chromophoric group which can be distinguished from other parts of the structure.

In the case of aldehydes and ketones, this chromophoric centre is the carbonyl group and is responsible for the characteristic absorption of these substances in the ultra-violet between 3500 and 2000 Å.U. It is not, however, the chromophoric group which is disrupted in the photochemical change : no oxygen whatever is formed in the decomposition. Rather do the effects pass to other parts of the molecule, and in the present instance it must be assumed that the energy passes in whole or in part from the carbonyl link to some point in the hydrocarbon chains, with the result that carbon monoxide and a mixture of paraffins are produced in nearly equivalent proportion. This result may be explained by the reactions :

$$CH_3 \cdot CO \cdot C_2H_5 \longrightarrow \cdot CH_3 + \cdot C_2H_5 + CO - ca.\ 80\ \text{kg.-cals.} \quad . \quad . \quad . \quad (3)$$

$$\cdot CH_3 + \cdot C_2H_5 \longrightarrow \tfrac{1}{3}(C_2H_6 + C_3H_8 + C_4H_{10}) \quad . \quad . \quad . \quad . \quad (4)$$

This is not the only possible change, however, for with methyl ethyl ketone, some 20% of the reaction probably follows the course (2) (p. 875), while with methyl butyl ketone, the analogous reaction (1) predominates almost completely.

The problem which presents itself is how the energy of the absorbed light quantum, which is at first located in the carbonyl group, is transmitted to the hydrocarbon chains. The quantity of energy involved is large : to split off the free alkyl radicals in reaction (3) requires some 80 kg.-cals. or up to 90% of the absorbed light quantum. To bring about

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* The thermal data used in this paper are based on the values already given by one of us (Norrish, *Trans. Faraday Soc.*, 1934, **30**, 103).

reactions (1) and (2) a high energy absorption is also required if we judge from the energy of activation of the unimolecular decomposition of butane, where some 65 kg.-cals. are required (Pease and Durgan, *J. Amer. Chem. Soc.*, 1930, **52**, 1262) for the thermal activation of the reaction $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3 \longrightarrow CH_3 \cdot CH:CH_2 + CH_4$.

The process by which free radicals are split off in, *e.g.*, methyl ethyl ketone, is to be conceived as entirely analogous to the Auger effect. Here, in the case of atoms, it sometimes happens that reversion from an excited to a normal state occurs without radiation, the whole of the energy being absorbed in the ejection of an electron from some other part of the atom instead. The extension of this idea to the case of molecules has been made by Herzberg, and it is not difficult to see the analogy in the present instance. Thus it happens that the energy of excitation of the chromophore becomes available for the dissolution of immediately contiguous bonds, and consequently the liberation of the alkyl groups directly attached to it.

It is noteworthy that for acetone the threshold of fluorescence occurs at *ca.* 3000 Å.U. (94 kg.-cals.), while photodecomposition persists to at least 3200 Å.U. (88 kg.-cals.). The energy absorbed in the ejection of both free radicals at once is 80 kg.-cals., so that, allowing for the usual short region of "overlap," there is a reasonable agreement with the above conception. It is alternatively possible that reaction (3) may take place in two stages, the primary ejection of one free radical, *e.g.*,

$$CH_3 \cdot CO \cdot C_2H_5 \longrightarrow CH_3 \cdot + \cdot CO \cdot C_2H_5 - 89 \cdot 5 \text{ kg.-cals.,}$$
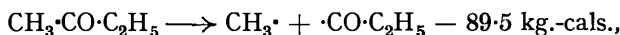
being followed by the spontaneous decomposition of the free acyl group :

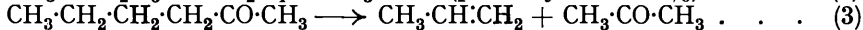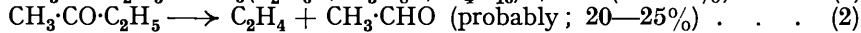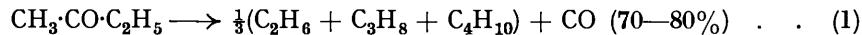$$C_2H_5 \cdot CO \cdot \longrightarrow C_2H_5 \cdot + CO + 9 \cdot 5 \text{ kg.-cals.}$$
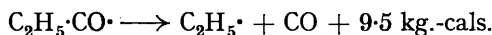
The value of the C—C link would appear to be in good agreement with the photochemical and fluorescence thresholds of acetone referred to above. The present results are unable to distinguish between the alternatives of simultaneous or successive ejection of hydro-carbon radicals, but if successive, the spontaneous decomposition of the free acyl radicals must follow rapidly, since there is no deficiency of carbon monoxide in the products such as would result from the fixation of acyl radicals by polymerisation or by combination with other ketone molecules.

For the case of methyl butyl ketone, where the energy passes to greater distances along the molecule, and ultimately decomposes the butyl chain to give propylene, the foregoing simple idea is inadequate. It is improbable that a simple Auger effect would extend to great distances within the molecule. We are, however, familiar in molecular physics with the conception of the "collision of the second kind," a process involving the radiationless transfer of energy from an excited molecule or atom to another with which it is in collision. Such collisions give rise to many well-known photosensitised reactions, such as those produced by excited atoms of mercury, neon, or xenon.

It may now be suggested that the large polyatomic molecule may vibrate periodically through a given phase, in which a radiationless transfer of energy between the excited chromophoric group and some other group within the molecule becomes probable. Such a condition is conceived as partaking of the same nature as a collision of the second kind between different particles. We shall describe this process as "inner sensitisation." The probability of a transfer of energy in this way will be dependent upon the existence of some degree of resonance between the hydrocarbon and the excited carbonyl groups, but the primary process of resonance, while it destroys the possibility of fluorescence, need not in every case be followed by chemical reaction; more than one effect may be possible, and thermal degradation may well be one of them. This could obviously occur if the probability of decomposition of the hydrocarbon chain when the energy of activation is directed at the critical spot, is not unity. It is thus readily understandable that such processes may lead to a quantum yield considerably less than unity in the continuous part of the spectrum, and that some molecules which absorb and do not fluoresce may escape reaction through a process of internal degradation.

SUMMARY.

The photochemical decomposition of the two mixed ketones, methyl ethyl ketone and methyl butyl ketone, has been investigated. Light of wave-length 3000—2200 Å.U. brings about the following decompositions :

$$CH_3 \cdot CO \cdot C_2H_5 \longrightarrow \tfrac{1}{3}(C_2H_6 + C_3H_8 + C_4H_{10}) + CO \;\; (70\text{—}80\%) \quad . \quad . \quad (1)$$

$$CH_3 \cdot CO \cdot C_2H_5 \longrightarrow C_2H_4 + CH_3 \cdot CHO \;\; (\text{probably}; \; 20\text{—}25\%) \quad . \quad . \quad . \quad (2)$$

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3 \longrightarrow CH_3 \cdot CH:CH_2 + CH_3 \cdot CO \cdot CH_3 \quad . \quad . \quad . \quad (3)$$

It is concluded that reaction (1) occurs by the scission of free radicals. Both this and reaction (3) require considerable quantities of energy, probably amounting to more than 50% of the absorbed light quantum, and the problem as to how this energy is transferred from the chromophoric group to the point of rupture is considered. With reference to (3), it is suggested that in polyatomic molecules with more than one group, a process of " inner sensitisation " akin to a collision of the second kind may occur, in which there is a radiationless transfer of energy from the one group to the other. The recipient group may then decompose or lose its energy as heat within the molecule.