

288. *Primary Photochemical Reactions. Part XI. The Photolysis of Aldehydes and Ketones in Paraffinoid Solution.*

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A study has been made of the photolysis of a number of aliphatic aldehydes and ketones in solution in medicinal paraffin and in *isooctane*. A differentiation of the primary processes into two types (I and II), analogous to those found in the photolysis of the vapour, was found. But although Type I in the case of aldehydes (breakdown to carbon monoxide and hydrocarbon) and Type II in the case of aldehydes and ketones (cracking of the hydrocarbon chain in the $\alpha\beta$ -position to the carbonyl group) remain unmodified by any secondary changes in solution, yet the course of Type I in the case of ketones is profoundly modified. This results from the fact that the free radicals first produced in the latter reaction become hydrogenated at the expense of the solvent paraffin at temperatures of 70–100°, with the production of equivalent unsaturation in the solvent. Since the hydrocarbons formed in the gas phase result from the combination of radicals, the hydrocarbons formed by hydrogenation of the radicals in solution are much simpler. A certain amount of aldehyde is produced by the hydrogenation of the acyl groups, though this decreases at the higher temperatures owing to the instability of the latter.

At room temperature the photolysis of ketones in solution by Type I reaction is completely suppressed. This readily follows from the fact that the hydrogenation reaction is strongly temperature-dependent, with the result that at the lower temperature the free radicals recombine by the operation of the Franck-Rabinowitch principle of primary recombination; *i.e.*, they find themselves constrained by a shell of solvent molecules and are caused to recombine before they can separate or be hydrogenated. In conformity with this idea, it is found that those reactions which yield molecules rather than free radicals (Type I for aldehydes, and Type II for aldehydes and ketones) occur as readily at or below room temperature as they do at 100°. The results completely confirm our earlier views as to the mechanism of the photolysis of carbonyl substances.

PREVIOUS papers of this series, which have been concerned largely with the study of the photolysis of aldehydes and ketones in the gaseous phase, have indicated a number of

important conclusions relative to the photolysis of polyatomic molecules. For the aliphatic carbonyl compounds these may be summarised as follows.

Photochemical decomposition occurs over the whole range of the carbonyl absorption band, lying approximately between the limits 3300—2000 Å. For the longer-wave part of the absorption band the life of the excited molecule may be considerable, up to 10^{-8} sec., as is apparent from the dual possibility of fluorescence and photolysis in some of the compounds studied, and in the lower homologues by the sharpness of the long-wave end of the spectrum. With decreasing wave-length, however, the life time of the excited state becomes reduced, and fluorescence is absent.

It has become clear that no correlation between diffuseness of the spectrum on the one hand, and fluorescence and predissociation on the other, such as is the case with diatomic molecules, can be established, a circumstance resulting from the long life period of the excited state of polyatomic molecules at the threshold of predissociation, as was first pointed out by Franck, Sponer, and Teller.

As the mass and the number of internal degrees of freedom of aldehydes or ketones are increased by the lengthening of the hydrocarbon chains, there arises the possibility of the internal degradation of the electronic energy of the excited state. Thus, even though the spectrum may be apparently continuous, and there is no fluorescence, the quantum yield of photolysis may be small, *e.g.*, acetone *ca.* 0.2, cyclohexanone 0.2. An extreme case of this is to be found in crotonaldehyde, whose vapour gives a continuous spectrum without any sign of fluorescence or photolysis (Blacet and Roof, *J. Amer. Chem. Soc.*, 1936, **58**, 73).

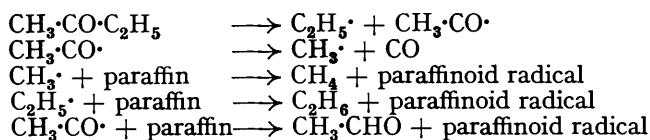
When photolysis occurs, either free radicals or finished molecules may result. With aldehydes and ketones there are two main types of decomposition, which have been referred to as Type I and Type II; in the former, carbon monoxide is eliminated with the formation of a hydrocarbon or hydrocarbons; in the latter, there is a cracking of the hydrocarbon chain in the $\alpha\beta$ -position to the carbonyl group with the formation of an olefin and a lower aldehyde or ketone. Both these types of decomposition can occur concurrently in the same substance. In addition, a third type of decomposition has been occasionally observed in which an olefin and an aldehyde are formed by a reaction involving cracking between the carbonyl group and the α carbon of the aliphatic group; *e.g.*, $\text{CH}_3\cdot\text{CO}\cdot\text{C}_2\text{H}_5 \longrightarrow \text{CH}_3\cdot\text{CHO} + \text{C}_2\text{H}_4$. The incidence of this reaction appears much rarer. It has been denoted as Type III.

The available evidence has hitherto pointed to the conclusion that with aldehydes the decomposition of Type I takes place mainly in one act: $\text{R}\cdot\text{CHO} \longrightarrow \text{RH} + \text{CO}$, while with ketones, free radicals are first produced according to the scheme $\text{R}\cdot\text{CO}\cdot\text{R}' \longrightarrow \text{R}'\cdot + \text{R}\cdot\text{CO}\cdot \longrightarrow \text{R}'\cdot + \text{R}\cdot + \text{CO}$, and then unite to form a mixture of the paraffins RR' , RR , and $\text{R}'\text{R}'$. With acetaldehyde, however, it has been shown that free radicals are formed in increasing quantity as the energy of the photolysing quantum is increased (Blacet and Roof, *ibid.*, p. 278). These conclusions have been verified in a very direct manner by Pearson (see, *e.g.*, *J.*, 1935, 1151).

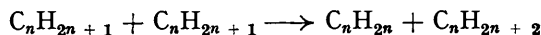
Decompositions of Type II, on the other hand, appear to take place in one act, with the primary production of the olefin molecule, *e.g.*, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3 \longrightarrow \text{CH}_3\cdot\text{CO}\cdot\text{CH}_3 + \text{CH}_2\cdot\text{CH}\cdot\text{CH}_3$. This process occurs more extensively with molecules possessing long hydrocarbon chains; it is indicative of a remarkable transmission of energy from the chromophoric carbonyl group, which is the seat of the light absorption, to a point some distance away where reaction occurs.

In the present and the following papers we describe a confirmation of the above conclusions, which puts them beyond the possibility of reasonable doubt, and disposes of various objections which have been raised. This confirmation is afforded by a detailed study of the photolysis of aldehydes and ketones in paraffinoid solution, and a comparison with the results already reported for their photolysis in the gaseous state. It is found that in such circumstances, free radicals if produced are readily hydrogenated at the expense of the paraffin if the temperature is above 70° , but at lower temperatures the rate falls off rapidly. Thus, with methyl ethyl ketone, methane, ethane, and carbon monoxide are produced by photolysis in solution in medicinal paraffin or *isooctane*, as compared with the ethane, propane, butane, and carbon monoxide produced in the gas phase. It is to be noted

also that there is a deficiency of methane and that acetaldehyde can readily be detected among the products. Thus, reactions of the following type occur :



In confirmation of this, a nearly equivalent amount of unsaturation can be titrated in the paraffinoid solvent after the removal of the products and the original ketone. It may be concluded that the large paraffinoid radicals produced by the above reactions exchange hydrogen freely with other paraffin molecules, until, when two radicals meet, this exchange results in a disproportionation and the production of an olefin; *e.g.*,



Similarly, from di-*n*-propyl ketone, propane is produced in paraffinoid solution, whereas hexane alone is formed in the gas phase. These observations are extended in an analogous way to other ketones, all of which show quite clearly that free radicals are produced by the primary process, and are then hydrogenated in solution at and above 70°, whereas in the gas phase they combine together to form the double radical hydrocarbons.

At room temperature, however, the free radicals are not hydrogenated by reaction with the solvent. There results a sharp drop in the reaction rate, and the photolysis is practically inhibited. For example, it is shown in the succeeding paper that the quantum yield of the photolysis of di-*n*-propyl ketone by Type I process in solution falls from *ca.* 0.3 at 70° and 100° to something less than 0.01 at 15°. This is sharply contrasted with the results in the gas phase, which show no such drop in quantum yield at room temperature. The other ketones studied give similar results; in all cases their decomposition is practically inhibited at room temperature. The explanation of this behaviour is found in a theoretical principle first enunciated by Franck and Rabinowitch (*Trans. Faraday Soc.*, 1934, **30**, 120), but hitherto without much experimental confirmation. According to their principle, two particles in contact in solution will make on the average 2 or 3 subsequent collisions before separating owing to the confining action of the solvent molecules. Thus free radicals or atoms liberated by a primary act are virtually caged together by the solvent molecules, and will almost inevitably recombine, unless they are stabilised by some secondary process before this can occur.

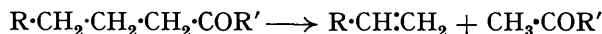
In the present instance, the two free radicals produced are a paraffinoid and an acyl radical. Stabilisation may occur at the higher temperatures, 70–100°, either by hydrogenation as already described or by decomposition: $\text{RCO}\cdot \longrightarrow \text{R}\cdot + \text{CO}$. Both these processes are, however, temperature-dependent, and at room temperature are so slow as to allow the recombination principle to operate powerfully. The free radicals almost invariably recombine, with the consequent inhibition of the photolysis.

With aldehydes, Type I reaction has also been found to occur in solution, but in this case there is but little unsaturation to be observed in the solvent; nor is any inhibition of the reaction in solution at room temperature to be detected—indeed, a ready decomposition of isovaleraldehyde occurs even as low as –80° in medicinal paraffin solution. These results show clearly that the aldehyde is decomposing mainly into molecules and not free radicals; for in these circumstances the principle of recombination would not operate, nor, since there are but few free radicals to react with the solvent, should we expect to find much unsaturation. Thus the earlier conclusion that the aldehyde under these conditions tends mainly to decompose to molecules in one act is confirmed.

Similar confirmation is obtained of the mechanism of photolysis according to Type II. With both aldehydes and ketones this has been found to occur in paraffinoid solution exactly as in the gaseous phase, yielding identical products and with a velocity that is but little changed. For example, it is shown in the next paper that the quantum yield of decomposition of di-*n*-propyl ketone according to Type II is nearly the same in solution

(0.20 at 68°) as in the gas phase (0.30 at 74°) and that it is only slightly affected by temperature.

Thus the circumstances attending the incidence of photolysis according to Type II are sharply contrasted with those associated with the incidence of Type I in ketones; it is clear, in view of the absence of any inhibition at room temperature, or of any equivalent unsaturation in the solvent, that a mechanism involving free radicals is excluded and that the process must take place in one act according to equation :



It is noteworthy that acetone forms the one exception to these results, for whereas it decomposes normally in the gas phase, no decomposition could be observed in decalin solution up to temperatures of 80°; rather, there is preferential reaction with the solvent, as shown by Bowen and Horton (J., 1936, 1685).

With this exception, we see that the primary act of photolysis, whether it be of Type I or Type II, is not materially influenced by the paraffinoid solvent, but that if free radicals are produced the course of the reaction may be profoundly modified by secondary reactions of the radicals or by the operation of the principle of recombination. It is evident that we have here a powerful tool for the detection of free radicals in a primary photochemical change.

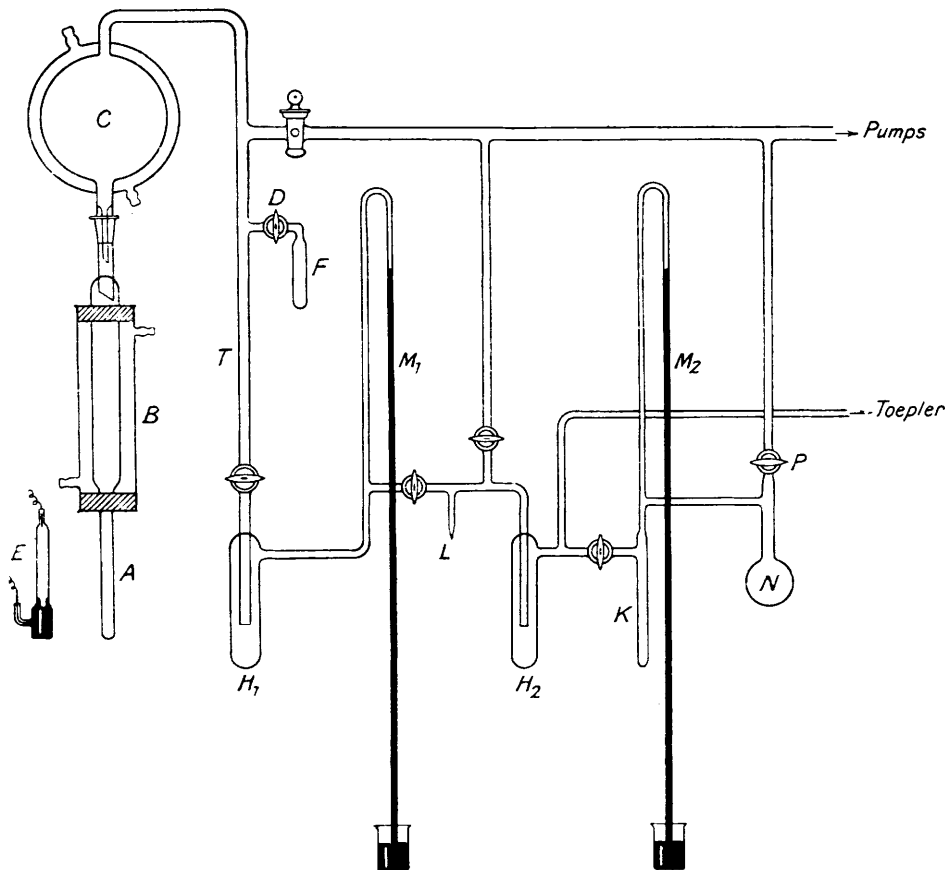
Another matter of importance emerges at this point, *viz.*, the origin of the low quantum yield of photolysis in the region of continuous absorption. Except in the case of the first two or three homologues of acetaldehyde, this is in no way connected with polymerisation, which, both with *cyclohexanone* and *di-n-propyl ketone*, has been shown to be negligible in amount. We have from time to time expressed the view that the inefficiency of the yield is rather to be ascribed to a process of internal degradation of energy of the excited molecules to vibrational and rotational energy associated with the numerous internal degrees of freedom of the polyatomic molecule. Against this it has been contended that the low yield is better explained by recombination of free radicals and by thermal degradation of excited molecules due to collision. Now, if recombination were the important factor, this explanation is greatly strained in the case of *crotonaldehyde*, where the quantum yield is nearly zero. It is also strained in the case of other ketones where there is good evidence that the acyl radical at temperatures above 70° decomposes spontaneously before it can make other collisions. Similarly, if deactivation by collision were the important factor, the quantum yield should depend markedly on pressure or the presence of inert gases, which is not so. It has not hitherto, however, been possible to distinguish unequivocally between these different possibilities. Our present results make such a decision possible. In a paraffinoid solvent above 70°, recombination cannot be the factor controlling the quantum yield, because, as we have seen, the free radicals react preferentially with the solvent molecules, and in those cases where it has now been proved that finished molecules result from the primary act, no such recombination is possible; the conditions under which recombination of radicals affects the process in the solution are clearly defined and predictable and lead to complete inhibition. Thus, the fact that, except where the principle of recombination operates, the quantum yield is very nearly the same in the gas phase as in solution, shows that the same major factor is operative in causing the low quantum yield in both cases. For obvious reasons this cannot be ascribed to degradation by collision—the quantum yield is nearly independent of the collisions of the solvent. We are left with the process of internal degradation, which alone can operate unchanged as we pass from gas phase to solution. That this is indeed the major factor can be seen by the fact that the quantum yields of Type I and Type II photolysis in the case of *di-n-propyl ketone* are reduced by only 19% and 38% respectively as we pass from gas to solution at 100°. It would seem that this is the proportion of deactivation which can be ascribed to external collision.

That internal degradation must be a quantised process is admitted; it may be asserted, however, that in view of the number and closeness of the vibrational and rotational levels in such large polyatomic molecules all possibility of structure disappears after the first few homologues have been left behind. This is beautifully shown by a comparative study

made by Professor Leighton of the structure of the absorption band of the carbonyl group in the lighter aldehydes (private communication): a progressive diffuseness of structure sets in, ending in continuous absorption, as the polyatomic molecule becomes more and more complex.

EXPERIMENTAL.

Procedure.—The apparatus used is illustrated in the figure, and is adapted from the type employed in the earlier work. It is suitable for the study of decompositions both in the vapour and in the liquid phase: when used for the latter the mode of operation was as follows. The liquid was contained in the quartz tube *A*, and could be maintained at any desired constant temperature by a water jacket not shown in the diagram. After introduction of the liquid into *A*, the latter was cooled in liquid air, and the apparatus completely evacuated by a two-



stage mercury-diffusion pump backed by a Hyvac pump; *A* was then warmed to the desired temperature, and irradiation started. The wide tube *B*, containing vapour of the carbonyl compound, was protected from the light. At the conclusion of the run the liquid in *A* was frozen, and the vapour in *B* condensed by cooling *A* in liquid air, following which any permanent gases produced were pumped off by the Toepler pump through two traps *H*₁ and *H*₂, also in liquid air. These gases constituted Fraction I. If medicinal paraffin was being used as a solvent (as was usually the case), *A* was next warmed to about 100°, and all volatile product completely distilled into the trap *H*₁. The paraffin is practically non-volatile at this temperature. Further fractionation was then performed by means of a series of different refrigerants. Convenient temperatures for the latter were found to be - 100° (liquid nitrogen-alcohol), - 78° (carbon dioxide-ether), 0°. At each temperature all volatile compounds were

removed. In this way the products were separated into several fractions, as shown for the specimen run on methyl ethyl ketone in Table I.

Gases were analysed by standard methods, a Bone and Wheeler apparatus suitable for dealing with small quantities of gas being used. The volumes of gases produced at the lower temperatures were frequently quite small. They were measured accurately by expanding the gases into a previously calibrated volume, and measuring the pressures exerted. Since the latter were of the order of 100 mm., they could readily be determined with sufficient accuracy. Liquid products were not pumped off, but were distilled directly into small weighed tubes attached by rubber connections to the outlet *L*. These tubes were subsequently sealed and reweighed. The liquids were identified by means of their physical and chemical properties.

When all volatile products and unchanged carbonyl compound had been distilled off, the non-volatile paraffin remained, and in many cases was found to have developed unsaturation during photolysis. This unsaturation was measured as follows. The residue was shaken several times with concentrated aqueous sodium bisulphite to ensure complete removal of reactive carbonyl compounds, then washed with water, and made up to a known volume with pentane. Measured volumes of this liquid were mixed with excess $N/50$ -bromine water and kept for one hour in the dark. Excess potassium iodide was then added, and the liberated iodine titrated with $N/100$ -thiosulphate in an atmosphere of carbon dioxide. Blank experiments were performed upon the mixtures of the original aldehyde or ketone and paraffin, the irradiation being omitted. In all cases it was found that the correction estimated in this way was very small. It is possible that in the case of the aldehydes the unsaturation was slightly overestimated on account of the presence of polymerised products in the paraffin residue. These would not be completely removed by the treatment with bisulphite and would probably be reactive to bromine water, and thus estimated as unsaturation. The figures given therefore represent the upper limits to the amount of unsaturation. The effect would be of much less importance with the ketones on account of their much lower tendency to polymerise and the non-reactivity of the polymer formed.

The medicinal paraffin used in these experiments was purified by shaking for some hours with sulphuric acid, washing with water several times, and then heating to about 100° in a vacuum to remove water and other volatile substances. The purified paraffin showed practically no absorption above 2350 \AA ., but beyond this wave-length a weak absorption was observable. The mercury arc used emitted comparatively little energy below 2350 \AA . The 10% solutions of the carbonyl compounds, on the other hand, exhibited intense absorption bands beyond 3100 \AA .; hence, the light absorbed by the solvent in the solution is quite negligible. The possibility of reactions produced by light absorption by the solvent was also investigated by irradiating the latter alone, under similar conditions to those used in the experiments to be described. There was no perceptible change after 5 hours; no gas was evolved, and no unsaturation developed.

Results.

In the following tables the collected results are given for the decomposition of the following compounds in paraffinoid solution: methyl ethyl, diethyl, methyl *n*-butyl, and di-*n*-propyl ketones, and acetaldehyde, *n*-butaldehyde, *isovaleraldehyde*, and crotonaldehyde. A specimen run for methyl ethyl ketone is set out in Table I; the details of the run are shown, indicating the different fractions into which the products were divided. In subsequent tables only the final results are given, volumes of products being expressed in c.c. at *N.T.P.*

Ketones.

Acetone.—This substance proved exceptional, and was the only ketone hitherto studied which gave no gaseous products on irradiation in solution. This was the case at room temperatures in *cyclohexane* solution, and at 70° in decalin. This is in accord with the findings of Bowen and Horton (J., 1936, 1685), who showed that, apart from slight reaction with the solvent, acetone is strongly resistant to photolysis in solution. The significance of this will be discussed later.

Methyl Ethyl Ketone.—In the full light of the hot arc there is only a very slow decomposition at room temperatures, ethylene being evolved. Between 60° and 100° , however, decomposition becomes rapid, and occurs mainly according to Type I. The gases evolved are predominantly methane, ethane, and carbon monoxide, together with small quantities of ethylene. The collected results are shown in Table II.

TABLE I.

Specimen run for methyl ethyl ketone.

A 10% solution in medicinal paraffin was employed. Irradiation for 4 hours, with the full light of the hot mercury arc. Temperature 63°.

Fraction.	Temp. of removal.	CO.	CH ₄ .	C ₂ H ₆ .	C ₂ H ₄ .	CH ₃ ·CHO.	Unsaturation developed in solvent (c.c. of olefin).
I	-190°	10.0	10.0	—	—	—	—
II	-100	—	—	41.8	3.7	—	—
III	-78	—	—	—	—	14.4	—
Totals		10.0	10.0	41.8	3.7	14.4	29.6

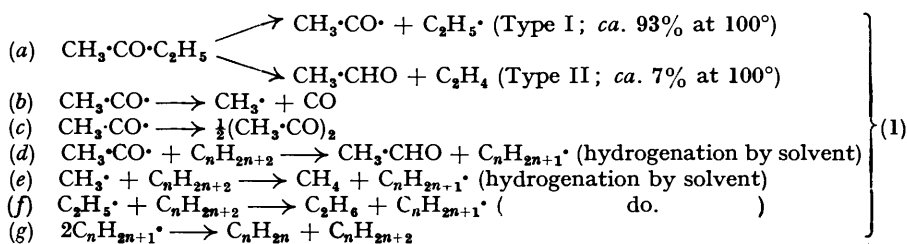
TABLE II.

Photodecomposition of methyl ethyl ketone in paraffinoid solution.

Full light of hot mercury arc used in all cases. Concentration of solution, 10% by volume in medicinal paraffin.

Temp.	Time of irradiation (hrs.)	CO.	CH ₄ .	C ₂ H ₆ .	C ₂ H ₄ .	CH ₃ ·CHO.	Unsaturation (c.c. of olefin at N.T.P.).	Yields per hr. C ₂ H ₆ .	C ₂ H ₄ .
20°	4.00	0.4	0.4	2.4	4.8	Present	—	0.6	1.2
63	4.67	10.0	10.0	41.8	3.7	14.4	29.6	9.65	0.85
70	2.42	6.5	6.7	24.5	1.9	Present	Not estimated	10.1	0.80
75	1.42	4.5	4.7	14.5	1.1	4.4	„	10.3	0.75
90	1.20	6.5	6.2	13.0	0.8	Present	„	10.8	0.65
100	2.00	16.8	16.9	22.2	1.2	2.5	„	11.1	0.60

It will be seen that, although in general the methane and carbon monoxide are equivalent, yet there is a high excess of ethane. This excess is bound up with the production of acetaldehyde in considerable quantities, and with the formation of small quantities of diketone which was detected in each experiment by the use of *o*-phenylenediamine, but not analysed. The acetaldehyde was isolated in a pure state by careful fractionation in a vacuum at -78°. The b. p.'s and f. p.'s of the liquids obtained were 20—22° and -120° to -124° respectively in all the experiments, while the corresponding figures for acetaldehyde are 20.2° and -121°. In each case the substance was miscible with water, and had the characteristic smell and reactions of acetaldehyde. The origin of the methane and ethane and of most of the acetaldehyde must be ascribed to the hydrogenation of CH₃·, C₂H₅·, and CH₃·CO· radicals by the solvent, but a little of the acetaldehyde, in view of the presence of ethylene, must have resulted directly, as is the case in the vapour-phase photolysis (Norrish and Appleyard, J., 1934, 807), by the alternative reaction C₂H₅·CO·CH₃ → C₂H₄ + CH₃·CHO. The hydrogenation of radicals was confirmed by a residual unsaturation which developed in the paraffin solvent and was measured as previously described after the volatile products and unchanged ketone had been removed. The results are simply explained by the following scheme.



The analytical figures show that, although all these reactions occur, their relative importance depends upon the temperature. For instance, the higher the temperature the greater the relative probability of 1(b) as compared to 1(c) and (d). The large excess of ethane over methane shows that the primary reaction involves the ejection of the ethyl rather than the methyl radical; the methyl radicals formed must thus mainly originate from subsequent decomposition of the acetyl radicals according to (b) above. This is in accord with the reluctance of methyl groups to split directly from acetone in solution. The values of the yields per hour show, further, that whereas the production of ethane (*i.e.*, Type I) is subject to a marked temperature coefficient, that of ethylene (Type II) has only a very small negative temperature coefficient.

According to the scheme above, there should be an approximate relation between the volumes of hydrocarbons and the acetaldehyde formed, and the corresponding unsaturation produced by the hydrogenation reactions. It follows that if the unsaturation be measured in c.c. of olefin at *N.T.P.*, then

$$\text{unsaturation} = \frac{1}{2}[\text{CH}_4 + \text{C}_2\text{H}_6 + \text{CH}_3\cdot\text{CHO} - \text{C}_2\text{H}_4].$$

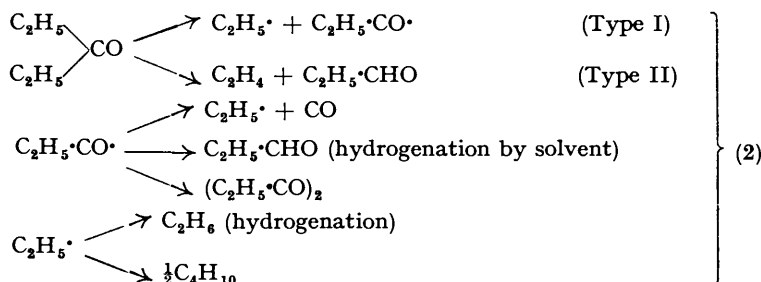
That this is approximately true is shown by the value of 29.6 c.c. for the unsaturation recorded in Table I, as compared to the value 24.1 calculated as above.

Diethyl Ketone.—Two experiments at 100° were performed with 10% solutions in medicinal paraffin. In each case irradiation was carried out with the full light of the hot arc.

Analytical results for diethyl ketone.

Period of irradiation (hrs.).	CO.	CH ₄ .	C ₂ H ₆ .	C ₂ H ₄ .	C ₄ H ₁₀ .
1.25	24.1	1.1	40.3	3.2	5.5
1 (lower intensity)	14.5	0.3	25.0	1.9	3.0

The results in the main are similar to those for methyl ethyl ketone. The predominant hydrocarbon product is ethane, small amounts of methane and ethylene also being formed. Positive results were obtained when the residues were tested for unsaturation, aldehydes, and diketones, but the amounts of the last two substances appeared to be much less than in the case of methyl ethyl ketone. This is reflected in the closer correspondence of the figures for CO and $\frac{1}{2}\text{C}_2\text{H}_6 + \text{C}_4\text{H}_{10}$. It is probably to be ascribed to the fact that $\text{C}_2\text{H}_5\cdot\text{CO}$ radicals have a lower stability than $\text{CH}_3\cdot\text{CO}$, and more readily undergo spontaneous decomposition into ethyl radicals and carbon monoxide. The experimental results are satisfied by the following scheme of reactions:



The origin of the methane obtained is not clear. It is produced, however, only in very small quantities, presumably by a secondary reaction liberating a few methyl groups. It may be calculated that, at 100°, approximately 87% of the decomposition occurs according to Type I, the residue involving the rupture of the molecule into ethylene and propaldehyde.

Methyl n-Butyl Ketone.—As in the gas phase (Norrish and Appleyard, J., 1934, 807), so in solution, methyl *n*-butyl ketone decomposes almost exclusively according to Type II. The results are given below.

Analytical results for methyl n-butyl ketone.

Temp.	Period of irradiation (hrs.).	Wave-length, A.	CO.	CH ₄ .	C ₄ H ₁₀ .	C ₂ H ₆ .	Unsaturation (c.c. of olefin at <i>N.T.P.</i>).	Yield per hr. of C ₂ H ₆ .	Type I, %.
18°	40	2536	ca. 0.05	ca. 0.05	ca. 0.05	7.0	0.2	(0.2)	0.7
20	20\	Full light of	0.2	0.2	0.3	30.0	0.3	1.5	0.7
85	20\	hot Hg arc	0.9	0.9	0.9	21.7	1.0	1.1	4.1

No diketone or aldehyde could be detected in any of the experiments. It will be seen that at room temperatures very small amounts of carbon monoxide, methane, and butane are produced, and the results are the same whether the full light of the hot mercury arc is used, or the radiation (mainly 2536 A.) from a lamp with cooled electrodes. The same is true at 85°, although there is a slight tendency for the amount of decomposition according to Type I to increase as the temperature is raised. It will be noticed that the effect of temperature on the Type II reaction is quite small. In accord with the almost complete absence of Type I, there is only a feeble development of unsaturation in the solvent, and this is roughly equivalent to the amount of Type I decomposition.

The results obtained with the last three ketones show quite clearly that the production of unsaturation is associated with the Type I reaction, but not with Type II. This proves that free radicals are produced in the former but not in the latter.

Di-n-propyl Ketone.—The results obtained are in accord with those recorded for previous ketones, but are somewhat more complicated because di-*n*-propyl ketone is capable of undergoing both Type I and Type II decompositions. This ketone has been studied in greater detail than the others, since it provides a means of investigating the effect of varying conditions of temperature and concentration upon both types of decomposition simultaneously. The results are given in Table III.

As in the cases of methyl ethyl, diethyl, and methyl *n*-butyl ketones, it is clear that the primary act is the same in the liquid and vapour phases. Thus, Type I leads to the production of alkyl and acyl radicals, which react in a manner similar to that already described under methyl ethyl and diethyl ketones, for whereas in the gas phase the propyl radicals combine to form hexane, in solution they are instead rapidly hydrogenated to propane. Over the whole range of temperatures there is a departure from a 2 : 1 ratio of the quantities of propane to carbon monoxide, the former being in considerable excess except at the highest temperatures where there is a slight deficiency. This deficiency of carbon monoxide may be accounted for by the hydrogenation of the acyl (C₃H₇·CO) radical to form an aldehyde, and also by its dimerisation to the diketone, (C₃H₇·CO)₂; for in all cases the presence of an aldehyde and an α-diketone could be detected in the solution after irradiation, the former by the rapid colorations produced when the liquids were shaken with Schiff's reagent, and by the reducing properties exhibited towards Fehling's solution, and the latter by the yellow colour developed by the solution at the lower temperatures, and its characteristic reaction with *o*-phenylenediamine. No diketone could be detected at 100°. The ratio (unsaturation, measured in c.c. of olefin)/(one-half propane produced) is shown in Table III to be approximately unity. At the lower temperatures, how-

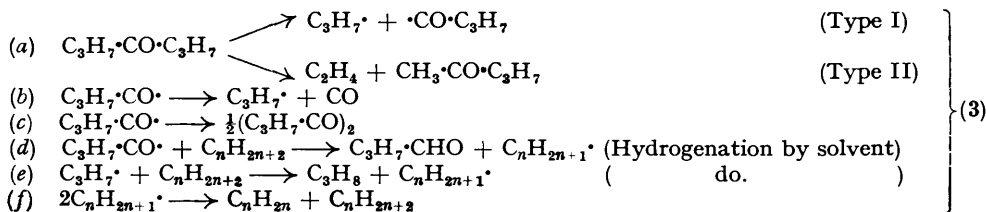
TABLE III.

Analytical results for di-n-propyl ketone.

Solutions in medicinal paraffin were used. The full light of the hot arc was employed except in the final experiment at 100° (marked *), which was carried out with 2536 Å. light.

Temp.	Concentration	Time of irradiation (hrs.)	CO.	C ₃ H ₈ .	C ₂ H ₄ .	C ₃ H ₈ - CO.		Unsatn. $\frac{1}{2}$ C ₃ H ₈	Yields per hr.	
						C ₂ H ₄	at N.T.P.		C ₃ H ₈ - CO.	C ₂ H ₄ .
0°	10%	9.67	0.93	8.77	98.5	0.07	5.00	1.23	0.76	10.2
5	"	6.25	1.05	8.38	62.5	0.12	—	—	1.17	10.0
10	"	6.50	1.84	13.28	64.0	0.18	—	—	1.76	9.9
15	"	4.67	2.10	14.0	45.2	0.26	6.15	1.15	2.54	9.7
20.5	"	8.25	5.45	32.5	28.3	0.34	20.0	1.23	3.80	9.5
30	"	3.25	4.35	24.2	29.8	0.67	—	—	6.11	9.2
40	"	4.50	9.36	47.5	40.4	0.94	—	—	8.48	9.0
55.5	"	—	16.5	65.0	42.0	1.16	—	—	—	—
60	"	2.42	10.8	32.9	19.6	1.13	19.8	1.20	9.13	8.1
60	1%	3.00	12.3	38.5	22.7	1.15	—	—	8.73	7.9
60	50%	—	5.7	16.8	10.5	1.06	—	—	—	—
60	100%	—	7.3	23.4	13.0	1.23	—	—	—	—
68	10%	—	19.4	40.6	21.3	1.00	—	—	—	—
85	"	2.50	24.9	45.0	18.5	1.09	24.8	1.10	8.04	7.4
100	"	1.17	15.4	24.5	8.2	1.11	11.4	0.93	7.78	7.0
100*	"	—	6.5	10.3	3.3	1.15	5.2	1.01	—	—

ever, it is rather larger, in agreement with the view expressed above that acyl as well as alkyl radicals are hydrogenated by the solvent. The main reactions occurring during photolysis may thus be represented as follows :



The lower the temperature the less the relative importance of the decomposition reaction (*b*) as compared with the dimerisation and hydrogenation reactions (*c*) and (*d*); consequently, the larger the ratio C_3H_8/CO . On the other hand, at high temperatures the decomposition occurs so rapidly that there is little hydrogenation and practically no dimerisation, so it would be expected that the ratio C_3H_8/CO would have the value 2. Actually, it is slightly less; this will be so if the life of the propyl radical in solution is sufficient to permit a small amount of recombination to form hexane. This will be discussed in detail in the following paper. If hexane formation be neglected (and it will be shown later that this is justifiable at low temperatures), the extent of the Type I decomposition is proportional to $(C_3H_8 - CO)$, and the table shows that, as in the cases of methyl ethyl and diethyl ketones, while this reaction occurs readily between 60° and 100° , its rate falls off to a very low value as 0° is approached. On the other hand, the Type II reaction, as shown by the figures in Table III for the yield per hour of ethylene, is only affected by temperature to a secondary extent, and this must be due, at least in part, to the increasing competition of Type I as the temperature rises. The methyl *n*-propyl ketone produced by the above reaction was not isolated, but evidence of its presence was provided by the fact that the solutions after irradiation produced a crystalline precipitate when shaken with concentrated aqueous sodium bisulphite (di-*n*-propyl ketone does not form a bisulphite compound). In addition, the residues responded to the iodoform test readily in the cold; the original ketone will respond to this test, but only with difficulty and on heating.

Inspection of Table III shows that the unsaturation measured is independent of the amount of Type II decomposition occurring. This is in agreement with the view previously expressed (p. 1534) that the Type I reaction alone is responsible for the production of unsaturation.

The figures in Table III also show that there is little change in the ratio of the two types of reaction as the concentration of ketone is varied from 1 to 100% at 60° . This is evident from the approximate constancy of the ratio $(C_3H_8 - CO)/C_2H_4$. Further, the experiment at 100° , in which the cold arc was used, indicates that the course of the reaction is not affected appreciably by the change in wave-length.

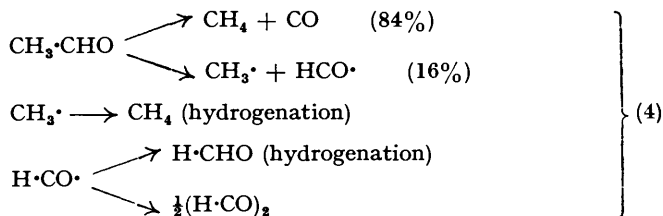
Aldehydes.

Acetaldehyde.—Two experiments on this aldehyde were performed; in each case a 5% solution in *cyclohexane* at 20° was irradiated by the full light of the hot arc for 12 hrs. The results are given below.

Analytical results for acetaldehyde.

H_2 .	CH_4 .	CO.	Unsaturation (c.c. of olefin at <i>N.T.P.</i>).
0.1	12.0	10.0	1.5
0.1	11.5	9.6	1.4

It will be seen that the amount of unsaturation developed is quite small compared to the volume of methane produced, showing that the greater part of the latter must arise directly, and not by hydrogenation of methyl groups. At the same time, the excess of methane over carbon monoxide indicates some decomposition into $CH_3 + H\cdot CO$ must occur, the alkyl group being hydrogenated to methane. In agreement with this, it was found that the liquids after irradiation possessed a yellow-green colour and the smell of glyoxal, while the *o*-phenylene-diamine test showed that a dicarbonyl compound was present; this, in conjunction with the remainder of the analysis, leaves no reasonable doubt that glyoxal was formed during irradiation by dimerisation of $H\cdot CO$ groups. The small amount of hydrogen formed makes it appear likely that there was no appreciable formation of hydrogen atoms during photolysis, since these would probably be rapidly hydrogenated by the solvent. The reactions occurring are represented by the scheme :



n-Butaldehyde.—The results of two experiments, in which 5% solutions of the aldehyde in medicinal paraffin were irradiated at 20° , are given in Table IV. The acetaldehyde produced

TABLE IV.
Analytical results for n-butaldehyde.

Wave-length, A.	Period of irradi- ation (hrs.).	H ₂ .	CH ₄ .	CO.	C ₃ H ₈ .	C ₂ H ₄ .	CH ₃ ·CHO.	CO/C ₂ H ₄ .	Unsaturation (c.c. of olefin at N.T.P.)
Full light of hot arc	4.25	0.2	0.2	12.3	11.8	2.8	Present but not estimated	4.4	1.5
2536	—	—	—	10.5	10.1	1.3	„	8.1	1.1

was identified by its b. p. (20—24°) and f. p. (ca. — 125°) and by its reactions in the ordinary way. As in the case of acetaldehyde, the unsaturation developed is quite small in comparison to the saturated hydrocarbon produced (C₃H₈). Moreover, in this case there is good agreement between the latter volume and that of carbon monoxide. There is thus no evidence for any appreciable formation of radicals during photolysis. It must be borne in mind that, as stated previously (p. 1536), the unsaturation was probably overestimated in the case of these aldehydes. The use of 2536 A. light instead of the hot arc does not increase the amount of hydrogen, or unsaturation, and hence does not appear to increase the probability of radical formation. In agreement with these conclusions, no dicarbonyl compound could be detected in either experiment. It will be seen that butaldehyde undergoes a Type II decomposition into ethylene and acetaldehyde. The ratio Type I/Type II, measured by the ratio CO/C₂H₄, is shown by the figures in Table IV to be markedly affected by wave-length, and to increase with decreasing wave-length.

isoValeraldehyde.—Five experiments were carried out with this aldehyde, with the results set out in Table V. In the first four runs, 5% solutions in liquid paraffin were employed, but in the fifth, at — 78°, a 5% solution in pentane was used.

The acetaldehyde was identified by its physical properties and chemical reactions. The b. p. and f. p. were 21—22° and — 123° to — 125° respectively in each experiment, and the latent heats of vaporisation calculated from the vapour-pressure curves were between 6.63 and 6.65 kg.-cals./g.-mol. The value for acetaldehyde is 6.62 cal./g.-mol. In the main the results

 TABLE V.
Analytical results for isovaleraldehyde.

Temp.	Wave-length.	Period of irradiation (hrs.).	H ₂ .	CH ₄ .	CO.	C ₃ H ₈ .	<i>iso</i> -C ₄ H ₁₀ .	CH ₃ ·CHO.	Unsaturation (c.c. of olefin).	CO/C ₃ H ₈ .
18°	Full light of hot arc	7	0.1	0.2	14.8	5.1	14.6	5.0	2.1	2.9
85	—	6	—	0.7	18.6	3.9	16.0	3.4	1.5	4.8
18	2536 A.	11.75	0.2	0.1	9.7	2.1	9.5	2.0	1.0	4.6
85	2536 A.	15.25	—	0.1	16.8	1.7	15.0	Present but not estimated	1.0	9.9
— 78	Full arc (low intensity)	4.5	—	—	1.4	0.8	1.3	„	—	1.8

resemble those obtained with *n*-butaldehyde. The amounts of hydrogen and unsaturation are small, showing that only a small fraction of the decomposition proceeds *via* free radicals. The production of appreciable amounts of radicals or hydrogen atoms would lead to the development of considerable unsaturation, comparable to the volume of saturated hydrocarbon (*isobutane*) obtained, whereas actually the ratio (unsaturation)/C₄H₁₀ does not exceed 0.3. As in the case of *n*-butaldehyde, use of the shorter wave-length (2536 A.) does not increase the amount of unsaturation with respect to the saturated hydrocarbons. The Type II reaction proceeds as in the gas phase, and consists in the splitting of the molecule into propylene and acetaldehyde. It is interesting to compare the effects of temperature and wave-length upon the two types of decomposition. The values of the hour yields of carbon monoxide (Type I) and propylene (Type II) are set out in the following table :

Hour yields for photolysis of isovaleraldehyde.

Temp.	Wave-length.	CO.	C ₃ H ₆ .	Temp.	Wave-length.	CO.	C ₃ H ₆ .
18°	Full arc	2.1	0.7	18°	2536 A.	0.83	0.18
85	„	3.1	0.6	85	„	1.1	0.11

while at higher temperatures, for the reasons stated above, it approximates more and more to the reaction

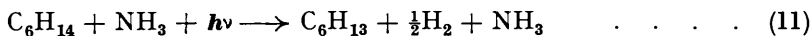


There is thus a progressive fall in the ratio of unsaturation to propane, the limiting value of (unsaturation, in c.c. of olefin)/½(propane) being unity.

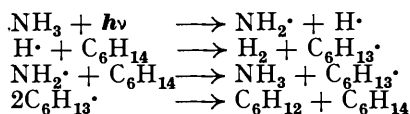
At still lower temperatures, however, the rate of hydrogenation of free radicals is greatly reduced. This process is strictly temperature-dependent, and is subject to an energy of activation the magnitude of which is estimated in the following paper. Thus, at room temperatures, the principle of primary recombination (see p. 1533) comes very markedly into play. The free radicals produced by the primary process are now confined in close proximity by the solvent molecules and, in the absence of hydrogenation, inevitably recombine. Perhaps the strongest confirmation of this conclusion lies in the fact that with the alternative Type II reaction, in which molecules rather than radicals are formed, there is no such falling off at room temperatures—indeed, the yield tends to diminish somewhat at the higher temperatures, owing to the increasing competition of the Type I change.

If we accept this view, and there seems little doubt of its correctness, we obtain added support for the conclusion that the Type I decomposition of aldehydes occurs in one act, without the liberation of free radicals, *i.e.*, $\text{R} \cdot \text{CHO} \longrightarrow \text{RH} + \text{CO}$. This conclusion has already been derived from consideration of the reactions in the gas phase (Norrish and Kirkbride, J., 1932, 1518; Bamford and Norrish, J., 1935, 1504); in solution, the absence of marked unsaturation at high temperatures, and the persistence of the reaction to low temperatures, can only be explained if the same conclusion is drawn. This is true, in the main at any rate, for wave-lengths as short as 2537 Å. If attention be focused on shorter wave-lengths, however, we think it likely that increasing numbers of free radicals may be formed, owing to the great increase of energy in the photolysing quantum.

It is of interest in the light of these results to reconsider Farkas's results (*Z. physikal. Chem.*, 1933, B, 23, 89); he found that, when a solution of ammonia in hexane is irradiated by light corresponding to the predissociation region of the former, there results sensitised decomposition of the hexane, with evolution of hydrogen, as represented by the scheme



It would now appear quite probable that, in view of the possibility of direct hydrogenation of radicals established by the present work, this result can readily follow from a decomposition of the ammonia, with the secondary reactions shown below :



In view of the fact that the predissociation of ammonia undoubtedly involves the splitting of the molecule, it would seem preferable to view the mechanism of the reaction in this way rather than as if it involved sensitisation. Indeed, it appears that no such case of sensitisation by collision with excited molecules has yet been established.

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