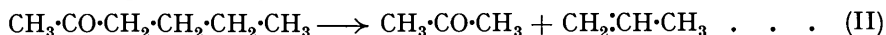**126.** *Free Radicals and Atoms in Primary Photochemical Processes.*
The Dissociation of Aliphatic Ketones : the Acetyl Radical.

By Harold H. Glazebrook and Thomas G. Pearson.

The photodissociation of ketones and aldehydes by light in the region 2000—3500 A. has been widely studied (Berthelot and Gaudechon, *Compt. rend.*, 1912, **155**, 204; Damon and Daniels *J. Amer. Chem. Soc.*, 1933, **55**, 2363; Norrish and Kirkbride, J., 1932, 1518; Norrish, Crone, and Saltmarsh, J., 1933, 1533; Norrish and Appleyard, J., 1934, 874), and it has been concluded (Saltmarsh and Norrish, J., 1935, 455), from the quantitative analysis of the reaction products and from the nature of the absorption spectra, that two types of decomposition are possible and usually occur simultaneously, the extent of each being governed by the symmetry of the molecule and the magnitude of the alkyl groups attached to the carbonyl. With the simpler ketones a change occurs typified by the dissociation of acetone :

$$CH_3 \cdot CO \cdot CH_3 \longrightarrow C_2H_6 + CO \quad \ldots \ldots \ldots \text{(I)}$$
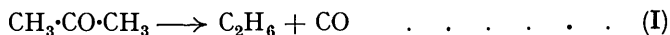
With higher ketones the hydrocarbon chain may break, as in the case of methyl butyl ketone, which decomposes mainly according to the equation

$$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3 \longrightarrow CH_3 \cdot CO \cdot CH_3 + CH_2 \vdots CH \cdot CH_3 \quad \ldots \quad \text{(II)}$$

It was also suggested (Norrish and Kirkbride, *Trans. Faraday Soc.*, 1934, **30**, 103) that in reactions of type (I) the primary act is a fission of the molecule into carbon monoxide and free alkyl radicals, a view confirmed by the characteristics of the fluorescence and absorption spectra of acetone vapour (Norrish, Crone, and Saltmarsh, J., 1934, 1456), and by the isolation of methyl, ethyl, and propyl radicals from among the primary products of the photolysis of dimethyl, diethyl, and dipropyl ketones (Pearson, J., 1934, 1718; Pearson and Purcell, J., 1935, 1151; 1936, 253; Pearson and Glazebrook, J., 1936, 1777). It is here shown that radicals also participate in the photolysis of methyl ethyl, methyl *n*-propyl, methyl *iso*propyl, di-*sec.*-butyl, and di-*tert.*-butyl ketones, and with improved technique, the smaller number of radicals in the dissociation of methyl butyl ketone has also been detected, contrary to the earlier observation (Pearson, J., 1934, 1718) that mirrors were scarcely affected, and to the conclusion that the concentration of radicals was less than one-twentieth of that of the methyl radicals resulting from acetone.

It has been found meanwhile that the activity of tellurium, arsenic, and especially lead and antimony mirrors, is diminished or completely inhibited by traces of oxygen admitted during or after their preparation. A mirror which is inactive to feeble concentrations of alkyl radicals may, however, be attacked, although slowly at first, in high concentrations such as exist in the thermal decomposition of acetone at 900°, presumably through the destruction of the oxide film by reaction with the radicals. The activity of a mirror also diminishes on standing, and to obtain reproducible results, it should be used within a few minutes of preparation. How far this is due to minute traces of oxygen given off from the walls of the apparatus, or to the crystallisation of the mirror, is not clear. The condition of the inner surface of the quartz tube exercises a considerable effect on the rate of recombination of the radicals. Tubes which have been in use for a considerable time, or have been cleaned with chromic acid mixture and insufficiently washed, or upon which there is a carbonaceous deposit, entirely prevent the passage of alkyl radicals. In the earlier experiments with methyl *n*-butyl ketone these factors were not appreciated, and only a relatively feeble source of ultra-violet light was available.

Norrish and his colleagues have estimated the contribution from reactions (I) and (II) in a number of cases from the composition of the final products of the photolyses, and we have determined directly the concentration of radicals present in these cases by comparing the times of removal of standard mirrors. The results are summarised in col. 4, Table I, Norrish's figures being added in col. 5. For purposes of comparison, we have assumed, with Norrish, that acetone dissociates wholly by way of radicals. The magnitudes of the values in cols. 4 and 5 are generally in agreement, and this is borne out by experiments in a different apparatus with di-*n*-propyl and di*iso*propyl ketones (Table II).

If reliance be placed on our relatively high value of the concentration of radicals in the dissociation of methyl ethyl and especially methyl butyl ketone, then either Norrish and his colleagues have made too low an estimate of the contribution from reaction (I), or processes other than the simple types (I) and (II) play a measurable part in the dissociation of ketones. For example, if an excited acetone molecule gives rise to ethane without the intervention of radicals, *i.e.*, $(CH_3)_2CO^* \longrightarrow C_2H_6 + CO$, this reaction would not be distinguishable from that involving dissociation into radicals by a method of assessment based on the analysis of the final reaction products. The possibility that the reaction might proceed in such a way was suggested by Damon and Daniels (*loc. cit.*), who did not, however, give free radicals any place in their reaction mechanism. Spence and Wild now include the intervention of active molecules without their dissociation into radicals as an essential part of their reaction scheme.
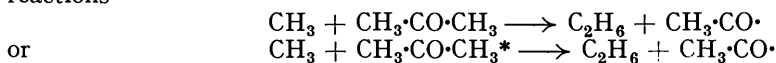
It is now generally recognised that the alkyl radicals participate in the reactions as a direct consequence of the primary fission of the molecule according to one of the processes $(CH_3)_2CO \longrightarrow 2CH_3{}^{\cdot} + CO$, or $(CH_3)_2CO \longrightarrow CH_3{}^{\cdot}CO^{\cdot} + CH_3{}^{\cdot} \longrightarrow 2CH_3{}^{\cdot} + CO$.

In the absence of diacetyl from the final products of the reaction and because of the equivalence of the amounts of carbon monoxide and ethane, it was concluded that both the bonds between the carbonyl group and the two methyls are broken simultaneously (*e.g.*, Saltmarsh and Norrish, *loc. cit.*; Bamford and Norrish, *J.*, 1935, 1505), but the intermediate formation of the acetyl radical was not excluded provided that it was short-lived and decomposed spontaneously under the experimental conditions (Norrish and Kirkbride, *Trans. Faraday Soc.*, 1934, **30**, 107; Pearson, *J.*, 1934, 1721).

Later, Barak and Style (*Nature*, 1935, **135**, 307) found diacetyl amongst the reaction products, an observation confirmed by Spence and Wild (*ibid.*, 1936, **138**, 206), who, working at room temperature, found the volume of ethane to be always 1·5 times that of the carbon monoxide, the deficiency being accounted for by considerable quantities of diacetyl. At 60°, however, they obtained approximately equal amounts of carbon monoxide and ethane, together with some methane. They suggested that the primary process is $(CH_3)_2CO^* \longrightarrow CH_3{}^{\cdot} + CH_3{}^{\cdot}CO^{\cdot}$, and that the acetyl radical is short-lived, especially at higher temperatures.

We confirmed the presence of diacetyl amongst the liquid products of the photolysis of acetone, but this is in itself only circumstantial evidence of the existence of the acetyl radical. We sought, therefore, to prepare lead acetate by allowing the products of the photolysis to impinge on lead peroxide; positive tests were obtained with the sensitive lanthanum nitrate–iodine reaction, but although the control experiments in the absence of ultra-violet light allowed the conclusion that some lead acetate had been produced, yet the results were not entirely satisfactory, for the concentrations tended towards the sensitivity limit of the test. Attempts were therefore made to establish the presence of the acetyl by indirect methods. We first confirmed Spence and Wild's observation that, although considerable amounts of diacetyl were produced when the walls of the apparatus were kept at 15°, yet no diacetyl whatever is obtained if the walls are maintained above 60°, although it is stable at this temperature. This is strong evidence that an unstable acetyl radical plays a part in the reaction, but it is just possible that different mechanisms obtain at different temperatures. We therefore removed the acetyl radical at room temperature by coating with tellurium the walls of the vessel in which the ketone was being irradiated. There were obtained only traces of diacetyl, but considerable quantities of dimethyl telluride. Control experiments showed that under the experimental conditions diacetyl passed unaffected through the apparatus.

The amounts of methyl and acetyl present during the photolysis of acetone were measured, and were comparable, so there is little doubt that below 20° the dissociation of acetone, with the formation of radicals, occurs largely according to the equation $CH_3{}^{\cdot}CO{}^{\cdot}CH_3 \longrightarrow CH_3{}^{\cdot} + CH_3{}^{\cdot}CO^{\cdot}$. The molecular ratio $CH_3{}^{\cdot}CO/Me$ is, however, greater than unity, and it was at first thought that the discrepancy could be accounted for by either of the reactions

$$CH_3 + CH_3{}^{\cdot}CO{}^{\cdot}CH_3 \longrightarrow C_2H_6 + CH_3{}^{\cdot}CO^{\cdot}$$

or $$CH_3 + CH_3{}^{\cdot}CO{}^{\cdot}CH_3{}^* \longrightarrow C_2H_6 + CH_3{}^{\cdot}CO^{\cdot}$$

but we found that methyl radicals yield no diacetyl with acetone whether in the dark or irradiated with ultra-violet light (see also Leermakers, *J. Amer. Chem. Soc.*, 1934, **56,** 1899—absence of chains in the photolysis of gaseous acetone).

Acetyl radicals prove to have a very short life compared with alkyl radicals even at room temperature, and combine amongst themselves or with methyl, react with acetone, or dissociate on each collision (or after very few collisions) with the walls of the quartz tube, so that they are unable to traverse appreciable distances from the irradiated zone.

EXPERIMENTAL.

Materials.—Acetone from the sodium iodide compound was dried with calcium chloride and fractionally distilled in a vacuum; b. p. 56·1°.

The other ketones were dried with calcium chloride and fractionally distilled through a bead column at atmospheric pressure, the fractions boiling between proper limits being collected : methyl ethyl ketone, b. p. 79·5°; methyl *n*-propyl ketone, b. p. 101·5—102°; methyl *iso*propyl ketone, b. p. 92—94°; methyl *n*-butyl ketone, kindly provided by Dr. G. A. R. Kon, b. p. 126—127·5°; di-*sec.*-butyl ketone, b. p. 163—164·5°. Di-*tert.*-butyl ketone, b. p. 148—150°, was prepared by the successive methylation of pinacolone (Haller and Bauer, *Compt. rend.* 1910, **150,** 582). It was found that the yield was increased from 17% to 40% by carrying out the reaction entirely in benzene instead of using ether for the first two stages. These purified specimens were redistilled in a vacuum immediately before use, with the rejection of about a quarter of each in head and tail fractions.

Alkyl Radicals from Aliphatic Ketones.—The apparatus used for detecting and measuring the concentrations of the radicals was similar to a previous one (J., 1935, 1153), but butyl phthalate manometers were employed. A single hot mercury-vapour arc (100 v., 4·5 amps.) served as a source of ultra-violet light. In a quartz tube of 12 mm. diameter, with the vapours entering the tube at 1—4 mm. pressure, and at velocities of 15—20 m./sec., opaque tellurium mirrors 2 mm. wide situated 4 cm. from the irradiated zone were removed in less than 4 mins. by the radicals from all the ketones mentioned above.

Repeated efforts were made to identify the radicals from di-*tert.*-butyl ketone. Unfortunately, the properties of the metal *tert.*-butyls are imperfectly known, nor do they lend themselves readily to identification, and although with mercury traces of an evil-smelling compound were obtained which combined with mercuric bromide to yield a substance which melted with decomposition in the range 105—110° (di-*tert.*-butylmercury bromide, m. p. 106°, decomp.), we do not regard the result as more than an indication. There was, however, no evidence of mercury-methyl, -ethyl, or -propyl, which should have been easily detected had they been present.

The concentrations of radicals occurring during the photolysis of a number of ketones were compared by observing the times of disappearance of standard tellurium mirrors situated at a constant distance along the quartz tube from the light source, the ketones being admitted to the tube at the same pressure. The results are recorded in Tables I and II.

TABLE I.

Pressure at beginning of tube, 0·7 mm. Hg.   Diameter of tube, 12 mm.

Ketone.	No. of expts.	Time of removal, t secs.	Relative concn. = $6500/t$.	Extent of type (I) reaction (Norrish *et al.*).
Dimethyl	5	65	100	100
Methyl ethyl	5	80	81	70—80
Methyl *n*-propyl	8	105	62	—
Methyl *n*-butyl	8	225	28	10

TABLE II.

[Calculated from data previously recorded (J., 1936, 1779).]

Pressure at beginning of tube, 0·9 mm. Hg.   Diameter of tube, 11·2 mm.

Ketone.	Time of removal, t secs.	Relative concn. = $3700/t$.	Extent of type (I) reaction (Norrish *et al.*).
Di-*n*-propyl	100	37	37
Di*iso*propyl	90	41	44

The Acetyl Radical.—The apparatus used was a modification of that previously described (J., 1936, 254, Fig. 2). Instead of the narrow joint *A*, a piece of quartz tubing equal in diameter to that at *D* was sealed on. This was fitted with a ground joint connected directly to a liquid-

air trap, and the whole was incorporated in an apparatus similar to that shown in Fig. 1, J., 1935, 1153, in place of the quartz tube XZ, so that the acetone vapour could pass in either direction through the quartz irradiation vessel. A single hot mercury-vapour arc was situated in C (Fig. 2, J., 1936, 254), and butyl phthalate manometers were used to avoid the presence of mercury in the apparatus. After the system had been thoroughly dried, acetone was introduced into the small fractionating vessel J containing phosphoric anhydride, out-gassed by cooling in liquid air and pumping, and kept for at least 12 hours at $-80°$. A small head fraction was removed before distilling the main volume of the liquid into a second vessel, and a few c.c. of tail fraction were left behind.

The acetone was streamed at a pressure of a few mm. of mercury through the quartz vessel of which the outer surface was covered with tin-foil, and irradiated. After passing backwards and forwards six times, the acetone had acquired a strong greenish-yellow colour and smelt of diacetyl. In a second experiment, after 52 passages with 30 c.c. of acetone, the liquid was fractionated from a vessel at $-90°$ to one in liquid air. The distillate was colourless until only about 1 c.c. remained. This residue was shaken with an excess of dinitrophenylhydrazine; a yellow precipitate was obtained, consisting largely of the acetone derivative, which was removed by extraction with boiling alcohol. An orange residue was left, too small to be recrystallised, which had m. p. 310—314° (m. p. of diacetyl derivative, 312°). During these experiments the cooling water was kept below 15°. They were repeated, but by using a slower rate of circulation of the water in the jacket, the walls were held at about 60°. No diacetyl could be detected after 10 passages of the acetone through the irradiated zone.

We tried to identify the acetyl radicals by allowing them to react with lead peroxide. In the first experiment, the lead peroxide was situated at A and D, and in later experiments, in view of the short life of the radical (see p. 571), the whole of the inner surface of the outer wall was covered with it. After 15 passages of acetone with the mercury arc running, the apparatus was dismantled, and the lead peroxide extracted first with 3 c.c. of distilled water, then separately with 5 c.c. of very dilute hydrochloric acid. The extracts were tested for acetate with lanthanum nitrate and iodine (Feigl, " Qualitative Analyse mit Hilfe von Tüpfelreaktionen," 1935, p. 408), and a positive reaction was obtained, but it was close to the sensitivity limit of the test (50γ per drop), and scarcely distinguishable from the results of the blank experiments.

In order to remove the acetyl radical at the room temperature, the inner surface of the outer wall of the irradiation vessel was completely covered with sublimed tellurium. This was done by cooling the outer wall of B with water while a Bunsen flame played up the centre C, and subliming tellurium from the bottom of B by means of a blowpipe flame. After 12 passages, so much of the mirror had been eaten away that it became patchy, and the experiment had to be discontinued. The product was a yellow liquid, smelling strongly of dimethyl telluride, which was removed by adding a solution of mercuric chloride in acetone, and filtering off the white flocculent precipitate of dimethyl telluride mercurichloride. The filtrate had a barely perceptible green colour. In another experiment, mercury iodide was used instead of chloride, and a canary-yellow precipitate was deposited identical in appearance with dimethyl telluride mercuri-iodide, again leaving only a very faintly green solution.

Evidently, the tellurium had effected practically quantitative removal of the diacetyl, probably through the simple dissociation $CH_3 \cdot CO \longrightarrow CH_3 \cdot + CO$, although an acetyl telluride may have been formed which we were unable to detect.

Since, after the removal of dimethyl telluride there is no other coloured product but diacetyl, it may be estimated colorimetrically. Two parallel series of experiments were therefore made in which the inner surface of the outer wall of the irradiation vessel was (a) left blank and (b) entirely covered with tellurium. In each complete experiment, ten passages of ketone were made under identical conditions, and the liquid products at room temperature were treated with 5 c.c. of a saturated solution of mercuric iodide in dry acetone.

After standing for at least 3 hours to ensure complete precipitation, the liquids were filtered through a weighed Pregl micro-filter. Any mercuri-iodide precipitate on the filter was washed three times with pure cold acetone, dried in a vacuum (Hyvac) at the room temperature for 5 minutes, and weighed. The clear filtrate was distilled from the excess of mercuric iodide, and the quantity of diacetyl in the distillate determined colorimetrically by comparison with a freshly prepared solution of diacetyl in acetone (2 mg. per c.c.). The results are shown below :

	$(CH_3 \cdot CO)_2$, mg.	$CH_3 \cdot CO$, mols. $\times 10^4$.	$TeMe_2,HgI_2$, mg.	CH_3, mols. $\times 10^4$.
Surface blank	4·8	1·11	none	none
Surface covered with Te	0·86	0·20	25·28	0·85

Before interpreting these data, it was necessary to establish that tellurium in the presence of ultra-violet light has no influence on diacetyl already formed, so the experiment was modified by having only the lower half of the surface of the irradiation vessel covered with the element. The product from ten runs was greenish-yellow and, after precipitation of the dimethyl telluride, was found to contain about half the amount of diacetyl yielded with the blank surface. It was noted that mercuric halides are without apparent action on solutions of diacetyl in acetone.

The results recorded above can only be given a roughly quantitative interpretation. If it is assumed that every acetyl radical formed yields diacetyl, and that every methyl or acetyl radical impinging on tellurium reacts to form dimethyl telluride, then it is clear that the molar quantity of acetyl produced is comparable with that of methyl.

The difficulty of reproducing experimental conditions in a large apparatus which must be dismantled, cleaned, and reassembled for each series of experiments cannot be overlooked.

To ascertain whether the large yield of acetyl was due to the reaction $CH_3\cdot + CH_3\cdot CO\cdot CH_3{}^*$ $\longrightarrow CH_3\cdot CO\cdot + C_2H_6$, the acetone was passed through a furnace at A, then rapidly cooled by running water over the outside of the tube, before entering the irradiated zone. Although there was a high concentration of methyl radicals in the gases leaving the furnace, the yield of diacetyl was not perceptibly increased above that obtained without the furnace. No diacetyl was obtained with the furnace, but without subsequent irradiation of the acetone, so that the reaction being sought is equally unlikely.

We tried to estimate the life-period of the acetyl radical by forming mirrors in the side arms of the apparatus at A and D (J., 1936, 254) just where the streaming gas leaves the irradiated zone. Although considerable amounts of dimethyl telluride were formed (12 runs, 7·26 mg. of dimethyl telluride mercuri-iodide), there was no perceptible diminution in the yield of diacetyl, so even under our conditions of high streaming velocity (19·2 m./sec. at beginning of tube) no acetyl leaves the irradiated zone, and recombination or decomposition must occur quantitatively in, or on the walls of, the irradiation vessel; hence, compared with the alkyl radicals, acetyl has a very short life (less than 10^{-4} sec.) in the presence of a silica surface, although on the average, acetyl radicals evidently survive more than 100 collisions with other molecules in the gas phase before combining on the walls to yield diacetyl.

An endeavour to refine the experiment by irradiating the acetone as it streamed through a straight quartz tube was unsuccessful because even after 28 runs (in the absence of tellurium) the greenish-yellow colour due to diacetyl was too faint for colorimetric comparisons, and extension of the number of experiments beyond 28 to fix each point made the method impracticably tedious.

SUMMARY.

The relative quantities of radicals present during the photolysis of acetone, methyl ethyl, methyl *n*-propyl, methyl *iso*propyl, methyl *n*-butyl, di-*n*-propyl, and di*iso*propyl ketones have been measured, and radicals have been obtained from di-*tert.*-butyl and di-*sec.*-butyl ketones.

The acetyl and methyl radicals are formed in comparable quantities during the photo-dissociation of acetone by ultra-violet light at room temperature. Acetyl radicals rapidly combine with one another to form diacetyl. Under our experimental conditions acetyl has a short life compared with the alkyl radicals; it is quantitatively decomposed on a silica surface at 60°, and is removed by tellurium at the room temperature.