375. *Free Radicals and Atoms in Primary Photochemical Processes. The Photo-dissociation of Aliphatic Ketones and Aldehydes.*

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BERTHELOT and GAUDECHON (*Compt. rend.*, 1910, **151**, 478; 1912, **155**, 207) showed that acetone is decomposed in ultra-violet light, yielding equivalent amounts of carbon monoxide and ethane, and Norrish and Appleyard (this vol., p. 874) obtained from the photolysis of methyl ethyl ketone almost equivalent amounts of ethane, propane, butane, and carbon monoxide, together with much smaller quantities of ethylene ($C_2H_5{\cdot}CO{\cdot}CH_3 \longrightarrow CH_2{:}CH_2 + CH_3{\cdot}CHO$). Norrish suggested (*Trans. Faraday Soc.*, 1934, **30**, 107) that the primary decomposition of methyl ethyl ketone cannot conform to an equation of the type found valid for aldehydes, *viz.*, $CH_3{\cdot}CO{\cdot}C_2H_5 \longrightarrow C_3H_8 + CO$, since in this case propane would be the only hydrocarbon formed. The primary change must involve free radicals, *e.g.*, $CH_3{\cdot}CO{\cdot}C_2H_5 \longrightarrow CH_3{\cdot} + C_2H_5{\cdot}CO{\cdot}$, and those of the latter type must decompose spontaneously in order to account for the quantitative formation of carbon monoxide and the absence of detectable quantities of diketone (Rice, *ibid.*, p. 168). The free hydrocarbon radicals then recombine to give the mixture of hydrocarbons found in practice.

This postulation of different mechanisms in the photolysis of ketones on the one hand and aldehydes on the other has, however, been questioned (*ibid.*, p. 118). The present work directly demonstrates that, in the photolysis of acetone, methyl ethyl ketone, and diethyl ketone, free alkyl radicals are produced, which may be detected beyond the irradiated zone by their action on mirrors of antimony, lead, and tellurium, whereby they form the corresponding metal alkyls. The half-life period of the radicals formed from acetone, $5{\cdot}3 \times 10^{-3}$ sec., is close to that determined by Paneth and Hofeditz (*Ber.*, 1929, **62**, 1335) for free methyl, *viz.*, $5{\cdot}8 \times 10^{-3}$ sec. The virtually unimolecular character of their association also strongly supports the assumption which is made, that the radicals effecting the removal of the metallic mirrors are methyls. If formed at all, acetyl radicals are unquestionably of very short life, certainly less than 10^{-3} sec.

In the photolysis of methyl butyl ketone, however, repeated attempts failed to disclose the presence of free radicals under similar conditions of irradiation. Free radicals, if formed in the *primary process*, have a concentration below one-twentieth of that of the methyl radicals resulting from acetone. This is in accord with the view of Norrish and Appleyard (*loc. cit.*) that the process here involved is almost quantitatively $CH_3{\cdot}[CH_2]_3{\cdot}CO{\cdot}CH_3 \longrightarrow CH_3{\cdot}CH{:}CH_2 + CO(CH_3)_2$. Acetone formed under the author's experimental conditions would be of such slight concentration in the irradiated zone that radicals arising from its photolysis might well escape detection.

The photo-dissociation of aldehydes has received much attention: formaldehyde (Bredig and Goldberger, *Z. physikal. Chem.*, 1924, **110**, 530; Bates and Spence, *J. Amer. Chem. Soc.*, 1931, **53**, 1694; Norrish and Kirkbride, J., 1932, 1518); acetaldehyde (Berthelot and Gaudechon, *Compt. rend.*, 1913, **156**, 68, 233; Bowen and Watts, J., 1926, 1607; Smith, *Carnegie Inst., Washington*, 1928, **27**, 178; Leighton and Blacet, *J. Amer. Chem. Soc.*, 1932, **54**, 3165; 1933, **55**, 1766); propaldehyde (Berthelot and Gaudechon, *loc. cit.*; Franke and Pollitzer, *Sitzungsber. K. Akad. Wiss., Wien*, 1913, **122**, 183); *iso*butaldehyde (*idem, ibid.*). These researches have shown the end-products to consist largely of a hydrocarbon and carbon monoxide, $R{\cdot}CHO \longrightarrow R{\cdot}H + CO$, and in the case of formaldehyde, hydrogen and carbon monoxide in 95% yield, $H{\cdot}CHO \longrightarrow H_2 + CO$.

Two primary processes have been suggested: that of Henri (*Leipziger Vorträge*, 1931, 131), Herzberg (*Trans. Faraday Soc.*, 1931, **27**, 378), and Mecke (*Nature*, 1930, **125**, 526) involves a free hydrogen atom, $H{\cdot}CHO + h\nu = H + COH$; and that of Norrish and Kirkbride (*Trans. Faraday Soc.*, 1931, **27**, 404) involves direct production of molecular hydrogen from formaldehyde, $H{\cdot}CHO + h\nu = H_2 + CO$, and of a hydrocarbon from higher aldehydes, $R{\cdot}CHO + h\nu = RH + CO$, a suggestion deduced from the unit quantum efficiency of the process, which would be unlikely if hydrogen atoms were present, as they would almost certainly become involved in secondary reactions with unchanged aldehyde molecules (Leighton and Blacet, *loc. cit.*). Later, Norrish (*Trans. Faraday Soc.*, 1934, **30**, 108) suggested that the process might occur in two stages, the first step, $R{\cdot}CHO \longrightarrow R{\cdot} + H{\cdot}CO{\cdot} - 89{\cdot}5$ Cals., being followed so rapidly by the second step, $H{\cdot}CO{\cdot} \longrightarrow H + CO$ (thermoneutral), that the R radicals and H atoms never get free of one another's sphere of influence, and are therefore eliminated as a single saturated hydrocarbon RH. In the present work, repeated attempts to establish the presence of free radicals or of hydrogen atoms in the photolysis of acetaldehyde and propaldehyde have been unsuccessful. There is, thus, a fundamental difference in the dissociation of aldehydes and ketones, of which Norrish and Kirkbride's mechanism may afford the explanation. The instability of the $R{\cdot}CO{\cdot}$ radical (if, indeed, it is formed) indicates that Norrish's modified mechanism may well be correct, as does the fact that the "magnitude of the limiting quantum necessary to the decomposition of such aldehydes is about 89 Cals. (3200 Å.U.), a value which agrees well with the thermal value for the C–C bond, but is inadequate for the rupture of the C–H bond" (*idem, ibid.*).

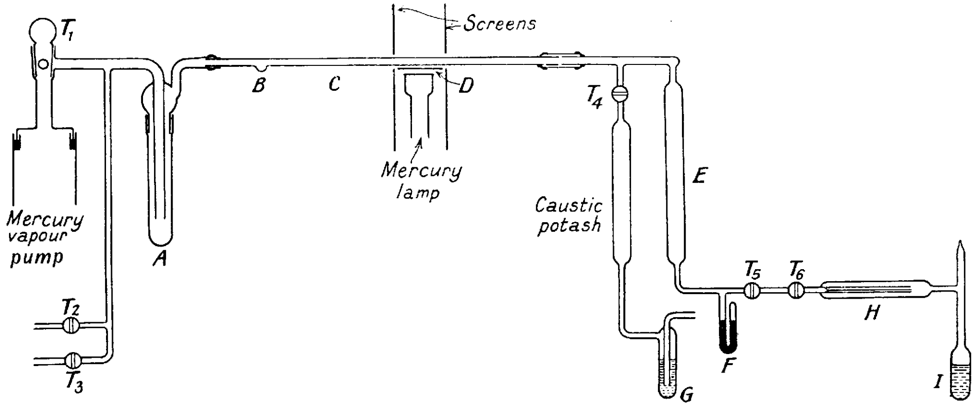
EXPERIMENTAL.

Macfarlan's B.P. acetone was dried and fractionated through a 15-inch column; b. p. 56·1°. Methyl ethyl ketone (300 c.c.) was converted into the bisulphite compound, air drawn through the suspension at 40—45° for 15 hours, the compound filtered off at room temperature, washed with ether and allowed to dry for 10 hours in the air, and the ketone liberated by steam-distillation, dried, and fractionally distilled with large rejections (yield 50 c.c., b. p. 79·5°). Diethyl ketone was available only in small quantity, and was redistilled before use. Methyl butyl ketone, prepared from *n*-propyl iodide and acetoacetic ester, was purified in the manner described under methyl ethyl ketone; b. p. 127°; semicarbazone, m. p. 122°. Acetaldehyde was prepared by the catalytic depolymerisation of pure (fractionally distilled) paraldehyde (b. p. 124·1°), and was itself fractionated; b. p. 21·2°. Propaldehyde was fractionally distilled, b. p. 49·5°.

The apparatus employed is shown in Fig. 1. The aldehyde or ketone contained in vessel *I* was admitted to the system *via* the capillary *H* and the rate-control taps T_5 and T_6, whence, after passing over a considerable surface of silver foil in *E* to remove mercury acquired from the manometer *F*, it entered the quartz tube *C*, and was subsequently frozen out in the trap *A* immersed in liquid air. The vacuum was maintained by means of a Kaye annular-jet mercury-vapour pump backed by two Hyvac oil pumps. To assist in fashioning the metal mirrors, hydrogen, prepared from A.R. zinc and pure hydrochloric acid, washed over 30% potassium hydroxide, and dried with potash pellets, was available at tap T_4.

In a typical experiment, the acetone in *I* was frozen in liquid air, and the apparatus exhausted with T_5 and T_6 open. T_6 was closed, and the acetone melted to release dissolved and imprisoned gas, which was subsequently removed by the pumps. This procedure was repeated three times. A mirror of suitable dimensions was formed at *C* with the aid of a small blow-pipe flame from the supply of metal in the depression *B* blown in the quartz tube (Pearson, Robinson, and Stoddart, *Proc. Roy. Soc.*, **1933**, **142**, 275). The quartz tube was shrouded with copper foil and wet cotton-wool, excepting a length of 5 cm. in which the vapour was to be exposed to the unfiltered radiation from a quartz-mercury vapour lamp (220 volts; 3 amps.) operating at a distance of 2·5 cm. from the tube. The pressure of acetone vapour was adjusted by means of T_6, and the vapour irradiated by raising the diaphragm *D* after the mercury lamp had been allowed to burn for 2 minutes. Despite the small diameter of the tube, 0·6 cm., the short length illuminated, 5·0 cm., and the low pressure obtaining within it, 0·5—2·5 mm. of mercury, mirrors of antimony opaque in ordinary daylight and 1·5 mm. in width were completely removed at distances up to 25 cm. (the maximum available) from the illuminated zone in times ranging from 12 to 60 minutes according to the thickness of the mirror and its proximity to the source. The products which condensed in the trap *A* after 2 hours with a heavy mirror situated 5 cm. from the source had a strong garlic odour similar to that of the antimony alkyls, whilst the acetone solution, faintly yellow at the room temperature, darkened in colour as it was cooled (compare Paneth, *Trans. Faraday Soc.*, **1934**, **30**, 179). The amount of volatile antimony compounds formed, estimated from the weight of mirror removed and the residue of antimony left after decomposing the products in the liquid-air trap, was too small (< 5 mg. per hour) for ordinary microchemical identification, particularly in the presence of 10—20 c.c. of acetone. Additional evidence was therefore sought by substituting tellurium for antimony. The products in the trap were slowly warmed to room temperature. The peculiar, dry, dusty smell of hydrogen telluride was not perceptible (b. p. −4·0°). The majority of the acetone was then removed by slow evaporation at the room temperature. The residue, a few drops of liquid, b. p. > 70° (dimethyl telluride has b. p. 85°), had the nauseating odour typical of alkyl tellurides. In a similar manner mirrors of lead, known to be unattacked by atomic hydrogen (Pearson, Robinson, and Stoddart, *loc. cit.*), were completely removed by the present aggressive agent.

FIG. 1.

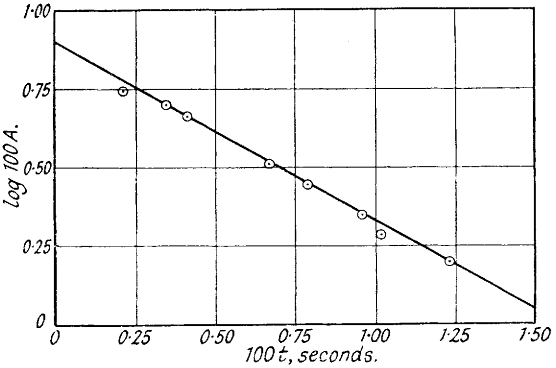


To confirm the inference that this agent arose through the photolysis of acetone, and not by a direct attack of warm acetone vapour, control experiments were carried out without the lamp, in which the tube was heated to about 50°, the temperature estimated to obtain during irradiation. A mirror 5 cm. from the heated zone, and so thin as to be transparent, was unaffected after 2 hours. A similar experiment in which the tube was heated to 150° likewise gave a negative result.

The life period of the free radicals from acetone was determined by comparing the times necessary for the disappearance of standard mirrors at different distances from the source (Paneth and Hofeditz, *loc. cit.*). The preparation of the standard mirrors was considerably facilitated by using as a standard for comparison a ring of soot smoked into a glass tube, but even with this aid, it was not possible to obtain times of disappearance agreeing more closely than the 10% obtained by previous workers. The accuracy of the final result was, however, increased by repeating each determination several times. The results are recorded in Fig. 2 and the table, in which L is the distance of the mirror from the nearer edge of the irradiated zone; t the time taken by the radicals to traverse the distance L; x the time of disappearance; A the activity $= 1/x$. The velocity of the gas stream, v, as it entered the tube was 12·3 m./sec., and the pressure, P, at this point 1·65 mm. of Hg. The average pressure gradient, a, in the tube was 0·002 cm. Hg per 1 cm. length of the tube. The time t was calculated from the formula used by Paneth and Lautsch (*Ber.*, 1931, **64**, 2702), *viz.*, $t = (X_2 - X_1)/V - a(X_2^2 - X_1^2)/2VP$, where X_1 and X_2 are respectively the distances of the irradiated zone and of the mirror from the beginning of the tube. Throughout the experiments, X_1 was kept close to 10 cm.

FIG. 2.

Life period of radicals from acetone.



Life Period of Radicals from Acetone.

No. of expts.	L, cm.	$t \times 10^2$, secs.	x, mins.	100A, mins.$^{-1}$.	log 100A.
4	3	0·210	18	5·56	0·745
6	5	0·345	20	5·00	0·699
3	6	0·411	22	4·55	0·658
3	10	0·665	31	3·23	0·509
2	12	0·787	36	2·78	0·444
2	15	0·961	45	2·22	0·347
1	16	1·017	52	1·92	0·284
3	20	1·232	63	1·59	0·202

In Fig. 2, log 100A is plotted against 100t, and it is seen that the points lie very nearly, but not quite, on a straight line. If the departure from linearity is real, it would lend support to the contention of Rice, Johnston, and Evering (*J. Amer. Chem. Soc.*, 1932, **54**, 3529) and Pearson, Robinson, and Stoddart (*loc. cit.*) that the disappearance of the radicals may occur, slightly at least, by way of a bimolecular process. That the first point lies off the line is explained by leakage of light through the screen, and reflexion along the tube. Assuming the unimolecular law to hold, the life period of the radicals calculated from these results is

$$\tau = 1/k = \frac{t_1 - t_2}{2{\cdot}3\,(\log A_1 - \log A_2)} = 7{\cdot}7 \times 10^{-3} \text{ sec.}$$

and the half-life period, $T = 0{\cdot}69\tau = 5{\cdot}3 \times 10^{-3}$ sec., which may also be read directly from the graph.

The absence of pronounced curvature in Fig. 2, the close agreement between the life period here determined and that of Paneth and Hofeditz, and the properties of the volatile substances formed by the action of the radicals on metallic mirrors are strong evidence that the aggressive agent is free methyl. If acetyl radicals are produced at all, then they must either (i) have a life period almost identical with that of methyl, an extraordinary coincidence, or (ii) be without action on antimony, a contention rendered improbable by their ultimate dissociation into carbon monoxide and ethane, or (iii), most probably, have a very short life and be reduced to a negligible concentration within a few thousandths of a second of their formation.

The photolysis of methyl ethyl ketone and diethyl ketone led to products which removed antimony mirrors at distances from the source up to 25 cm. in similar but rather longer times. With diethyl ketone the time increased more rapidly with the distance from the source than in the case of acetone, suggesting that radicals of somewhat shorter life were involved (see life period of free ethyl, Paneth and Lautsch, *loc. cit.*).

The products from methyl butyl ketone failed to remove a standard mirror, and two experiments were therefore carried out with very light, almost transparent, mirrors situated 5 cm. and 2 cm. respectively from the nearer edge of the source, in which the ketone was irradiated for 2-hour periods. In the first case the mirror was unchanged, and in the second it possibly suffered a slight loss in intensity. Since such a mirror would have been completely removed by similarly treated acetone in less than 12 minutes, the quantity of radicals cannot exceed 2½% of those present in the dissociation of acetone. To ensure that the apparatus was functioning properly, each of the above experiments was preceded and followed by a control run with acetone.

Three separate experiments with acetaldehyde and three with propaldehyde at 0·5, 1·5, and 2·0 mm. failed to exhibit perceptible removal of metal from the thinnest antimony mirrors (reactive both to alkyl radicals and to atomic hydrogen) situated 3 cm. from the illuminated zone in 3 hours, although the seven check runs with acetone which controlled the series led to the complete removal of much denser mirrors in 17 minutes. Assuming, as an outside estimate, that the mirrors employed with the aldehydes would be removed in 12 minutes by acetone, and that the limit of perceptible intensity change is not less than 25%, the concentration of radicals must again be less than 2½% of that present during the photolysis of acetone.

SUMMARY.

(1) Free alkyl radicals have been isolated from the primary products of the photolysis of acetone, methyl ethyl ketone, and diethyl ketone, and characterised by their reactions with antimony, tellurium, and lead.

(2) Free radicals could not be detected in the photolysis of methyl butyl ketone, acetaldehyde, or propaldehyde.

(3) These findings confirm the mechanism suggested by Norrish and Kirkbride and by Norrish for the photolysis of aliphatic aldehydes and ketones.

(4) The half-life period of the radicals from acetone under the experimental conditions is $5{\cdot}3 \times 10^{-3}$ sec.

The method is now being applied to a large number of photochemical reactions, and with the provision of a more powerful source of ultra-violet radiation it is hoped to identify by direct chemical tests the primary products of the reactions.

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