

**272.** *Free Radicals and Atoms in Primary Photochemical Processes.  
The Photodissociation of Aliphatic Aldehydes and Ketones.*

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It was recently shown (J., 1934, 1718) that, during the photodissociation of acetone, methyl ethyl ketone, and diethyl ketone, free radicals were formed which attacked mirrors of antimony, tellurium, and lead, yielding unpleasant-smelling liquids similar in all respects to metal alkyls, although with the technique then available it was impossible to identify them unambiguously. It was indicated that the radicals from acetone were probably free methyl: they had a half-life period of  $5.3 \times 10^{-3}$  sec., in good agreement with the 5.8 and  $5.2 \times 10^{-3}$  sec., obtained respectively by Paneth and Hofeditz (*Ber.*, 1929, 62, 1335) and Paneth, Hofeditz, and Wunsch (this vol., p. 375).

We now find that the radicals from the photolysis of acetone are indeed free methyl, and react with tellurium to form dimethyl telluride and ditelluride; with mercury to form dimethylmercury, identified as methylmercury bromide; and with arsenic to give trimethylarsine, identified as its monomercurichloride. Diethyl ketone gives ethyl, which combines with arsenic to yield triethylarsine, identified as its dimercurichloride.

The great difficulty of identifying minute quantities of radicals in the presence of a larger amount of condensable vapour led us to examine in some detail the various methods proposed for this purpose. Rice, Johnston, and Evering (*J. Amer. Chem. Soc.*, 1932, 54, 3529; 1934, 56, 2105) allowed the radicals to combine with mercury, and passed the resulting mercury dialkyls into mercuric chloride or bromide solution. The mixture of mercury halide with methyl and ethyl mercurihalides was then separated into its constituents by vacuum sublimation. We confirm that the reactions are quantitative, and the separation

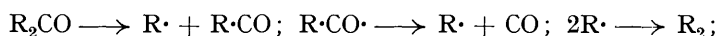
effective, but we abandoned the method because mercury diffused into the heated or irradiated zones. For the same reason, the use of iodine and carbon tetraiodide (Simons and Dull, *ibid.*, 1933, **55**, 2696) is questionable, although, in agreement with Willstätter and Utzinger (*Annalen*, 1911, **382**, 148), the alkyl iodides, even in minute amounts, could be identified as the tetra-alkylammonium iodides, or even more conveniently, after reaction with dimethylaniline, as the phenyltrialkylammonium iodides. The formation of sodium alkyls (Simons and Dull, *loc. cit.*), followed by treatment with alcohol and identification of the resulting hydrocarbon, suffers from disadvantages: the hydrocarbons formed are difficult to characterise, and not only does sodium readily attack quartz, but it is difficult to preserve its surface in an untarnished, reactive condition. The separation by fractional distillation or condensation of the liquid alkyls of zinc (Paneth and Hofeditz, *Ber.*, 1929, **62**, 1335), antimony, and arsenic (*idem, ibid.*; Paneth and Loleit, this vol., p. 366) was not suited to the immediate problem, since sharply-cut fractions could not be obtained in the presence of large excesses of ketone.

It was evidently desirable to devise an apparatus in which the ketone could be used a number of times, with consequent accumulation of the yields. The fixing of the metal alkyls as non-volatile addition products with mercuric chloride proved satisfactory. We find that, like those of arsenic, both antimony and tellurium alkyls form compounds by the direct addition of mercuric halides, but since only the compounds with arsenic have been described by other workers (Trochimovski, Buezvinski, and Kwapiszewski, *Rocz. Chem.*, 1928, **7**, 423; Challenger, Higginbottom, and Ellis, *J.*, 1933, **95**; Challenger and Ellis, this vol., p. 396), we preferred to use them. Alkylarsines combine quantitatively with mercuric chloride to yield compounds which may be recrystallised from hot water, and the methyl derivatives sublime in a vacuum without decomposition. The ethyl analogues decompose during sublimation, and the simultaneous action of different alkyl radicals produces a mixture of trialkylarsines of which mercurichlorides are difficult to separate.

The formation of the red liquid dimethyl ditelluride, advocated by Rice and Glasebrook (*J. Amer. Chem. Soc.*, 1934, **56**, 2472) and Rice and Dooley (*ibid.*, 1935, **57**, 2747) for the identification of methyl radicals, is satisfactory, but occurs only when hot tellurium mirrors are employed, and even then is accompanied by dimethyl telluride. In the cold, the latter is the main product. This phenomenon is reminiscent of Paneth and Loleit's finding (*loc. cit.*) that, whereas at low temperatures methyl radicals react with arsenic and antimony to form the trimethyl compounds, yet high temperatures favour the production of the more highly condensed cacodyls. It is suggested that the higher temperature allows the volatilisation of dimethyl ditelluride before additional radicals are able to produce dimethyl telluride.

In the earlier work (*loc. cit.*) metallic mirrors were not attacked by the products from photolysing acetaldehyde. We now find that free radicals are nevertheless present, and the previous failure to observe them was due to the protection of the mirrors by a film of polymerised aldehyde; for if, *e.g.*, tellurium mirrors are heated to such a temperature that the polymeride cannot deposit, they are readily removed, with the formation of methyl tellurides. Leermakers (*J. Amer. Chem. Soc.*, 1934, **56**, 1537) has shown that above 80° the photolysis of acetaldehyde is a chain reaction which may be induced and propagated by the methyl radicals from photolysing acetone. In subsequent experiments, therefore, we cooled the irradiated portion of the tube, and restricted the heating to the immediate neighbourhood of the mirrors, which were completely removed, so that, even if the radicals which reached them were the secondary products of a chain reaction, this at least had been initiated by radicals formed at the room temperature.

Under identical conditions of temperature, pressure, and irradiation, we find that acetone produces 2.07 times as many radicals as acetaldehyde, which implies (see p. 1156) that, in the photolysis of equivalent quantities of these compounds, 6 times as many radicals participate in the former process as in the latter. Although this value is approximate (see p. 1156), its order must be correct, and it confirms Norrish's view (*Trans. Faraday Soc.*, 1934, **30**, 107) that there is a fundamental difference in the photolysis of ketones and aldehydes, the former decomposing essentially by way of radicals :

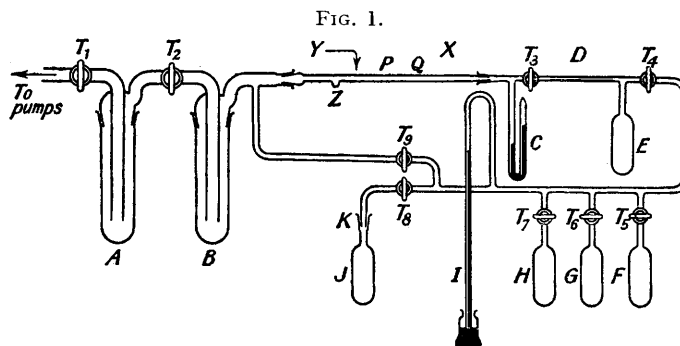


and the latter giving a hydrocarbon and carbon monoxide in one primary act:  $R\cdot CHO \longrightarrow RH + CO$ . Terenin (*Nature*, 1935, **135**, 543) has shown that such a primary process as that suggested for aldehydes is not impossible. Nevertheless, the alternative mode of decomposition of aldehydes which proceeds *via* free radicals plays a definite, though less important, rôle even at room temperature. The findings are, therefore, also in harmony with Leermakers's conclusions (*loc. cit.*) that radicals participate in the dissociation of aldehydes, setting up chains so that the quantum yield is as high as 300 at  $309.5^\circ$ . At room temperature, however, where the quantum yield from the chain reaction falls to 0.03, against an over-all yield of 0.20, their influence is but slight.

Finally, the results accord with the small quantities of hydrogen present in the final products from the photolysis of aldehydes. Thus, Leighton and Blacet (*J. Amer. Chem. Soc.*, 1932, **54**, 3165; 1933, **55**, 1766) detected it in the products from butaldehyde and found about 5% in those from propaldehyde, and Leermakers (*loc. cit.*) obtained 3% from acetaldehyde, quantities of the order to be expected from the 17% of aldehyde which yields free radicals ( $R\cdot CHO \longrightarrow H\cdot + RCO$ ;  $RCO\cdot \longrightarrow R\cdot + CO$ ;  $2H\cdot \longrightarrow H_2$ ;  $2R\cdot \longrightarrow R_2$ ).

## EXPERIMENTAL.

Acetone ("AnalaR," or from the sodium iodide compound) was dried over anhydrous sodium sulphate, or quickly over phosphoric anhydride, and fractionated in a high vacuum. Diethyl



ketone (B.D.H.) was fractionated in a 2' 6" bead-column, and the fraction of b. p.  $100.8\text{--}101.4^\circ$  transferred to the apparatus, wherein it was again fractionated in a high vacuum. Acetaldehyde was prepared by warming pure liquid paraldehyde with 2 drops of dilute sulphuric acid in an all-glass apparatus fitted with a 2' 6" bead-column. The portion distilling between  $21^\circ$  and  $22^\circ$  was refractionated through the same column, the fraction of b. p.  $21.2^\circ$  being collected and refractionated in a high vacuum.

The apparatus previously used (*loc. cit.*) was modified (see Fig. 1) to allow of (a) the circulation of the ketone so that a small quantity could be repeatedly irradiated and the alkyls accumulated, (b) the fractionation of original liquids or the products from the experiments, and (c) two different liquids being passed successively through the apparatus without exposure to the air. In a typical experiment, the previously fractionated acetone was frozen out in *J*, and the apparatus completely evacuated. The acetone was melted to release dissolved and imprisoned gas,  $T_4$  and  $T_9$  were closed, and the acetone fractionated between *F*, *G*, and *H*. The head and tail fractions were distilled back into *J*,  $T_8$  was closed, and the acetone removed from *J*, which was then charged with 0.2 g. of mercuric chloride, replaced in the system, and evacuated by suitable manipulation of the taps. The purified acetone was then distilled into *J* and allowed to warm to room temperature in order to dissolve the mercuric chloride, and thus provide for its distribution over the surface of *J* on subsequent evaporation of the solvent. An arsenic mirror of suitable dimensions was formed at *Y* from the metal contained in the depression *Z*. The quartz tube was swathed in wet cotton wool, except the length *PQ* of 10 cm., in which the vapour was to be exposed to the unfiltered radiation from two hot quartz mercury-vapour arcs (220 volts; 3 amps.) operating 1—2 cm. on opposite sides of the tube. The pressure of acetone vapour was adjusted by means of the combined aid of the tap  $T_3$  and the capillary *D*, and the vapour irradiated by striking the arcs. After the whole of the acetone had passed through the tube and collected in the liquid-air trap *B*, the arcs were extinguished,  $T_2$  was closed, and the

whole of the condensate distilled back into *J* via  $T_3$ ;  $T_3$  was then closed, the contents of *J* allowed to warm to room temperature, and after the lapse of a period to permit the complete formation of the mercurichloride, the cycle of operations was repeated until a suitable quantity of this compound had been accumulated (usually ten runs).

*The Photolysis of Acetone.—Arsenic mirrors.* The mercurichlorides from 7 runs with acetone over arsenic mirrors were freed from acetone by vacuum distillation, extracted with 7 ml. of boiling water, filtered, and set aside to crystallise. The crystals were filtered off, washed with several small quantities of water, and dried at room temperature in a vacuum desiccator over calcium chloride. The m. p.'s of two small portions were determined by a micro-method; melting commenced at 165° and was complete at 210°. The material was then fractionally sublimed in a vacuum and behaved as pure trimethylarsine mercurichloride (transition temp. 184°, m. p. 223—225°). An authentic specimen, recrystallised from hot water and sublimed under identical conditions, had transition temp. 184°, m. p. 224—226°. A mixture of equal parts of the two specimens was completely sublimed on to a cover-slip (transition temp. 184°, m. p. 224—226°).

*Antimony mirrors.* The products condensed in the liquid-air trap were evil-smelling liquids, completely deodourised by mercuric chloride. Attempts to separate the liquids by fractional distillation were unsuccessful, since the products appeared to distil with the acetone vapour. It was clear, however, that there were two liquids present, the more volatile being colourless, and the less volatile yellow, at liquid-air temperature. With heated mirrors, the latter compound was formed in abundance, and condensed in a yellow ring above the liquid-air level. It had the property of bisdimethylantimony of changing from a red solid to a pale yellow liquid just below the room temperature (m. p. 17.5°), whereas on cooling in liquid air the colour was lighter than that at the room temperature (Paneth and Hofeditz, this vol., p. 366).

*Tellurium mirrors.* Cold tellurium mirrors yielded a pale yellow liquid after removal of acetone by fractional distillation; it had b. p. (micro) 84—94°, and exhibited the persistent nauseating odour of dimethyl telluride (b. p. 92°). In certain experiments with hot mirrors (100—200°), a non-volatile red oil with all the properties of dimethyl ditelluride was obtained.

*Mercury.* For examining the reaction of the radicals with mercury, we used an all-glass modification of Rice's apparatus (*Trans. Faraday Soc.*, 1934, 30, 167). The quartz tube was led into it by way of a tightly-fitting sleeve-joint sealed with picein. The products were passed into a trap containing mercuric bromide cooled in liquid air. At the conclusion of the run, the products in the trap were allowed to attain room temperature, and after standing for a suitable period, the acetone was distilled off, and the solid residue fractionated by vacuum sublimation. The first fractions melted at 160° (methylmercury bromide has m. p. 162—164°; Rice, Johnston, and Evering, *loc. cit.*, 1932).

*Iodine.* The apparatus was the same as that used in the experiments with mercury, but the condenser was filled with alcohol cooled to — 60° with carbon dioxide snow, and the liquid-air trap was not charged with mercuric bromide. The total products were melted, treated with a drop of trimethylamine or dimethylaniline, shaken with an excess of freshly precipitated silver to remove free iodine, filtered, and kept for 24 hours at the room temperature, the acetone being then distilled off in a vacuum. Unfortunately, the residual oily droplet could not be crystallised, and the very small yields were apparently contaminated with products resulting from the action of iodine on the acetone. Furthermore, the method was rendered impracticable by the ease with which the iodine diffused over all parts of the system, even against the gas stream.

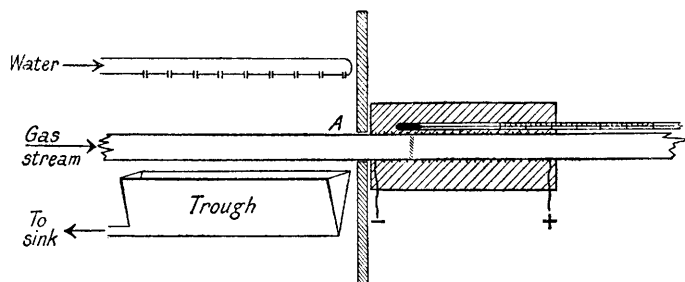
*Photolysis of Diethyl Ketone.—Arsenic mirrors.* Ten runs were made with this ketone, the volatile products being collected in mercuric chloride. A small residue of non-volatile oil left in the liquid-air trap appeared to be cyclic pentaethylpentarsine (Paneth and Loleit, this vol., p. 370). The mercurichlorides were extracted with 5 ml. of boiling water, filtered from insoluble residue, cooled, and left in a vacuum desiccator over calcium chloride. Crystallisation was allowed to continue until the characteristic crystals of mercuric chloride appeared at the edge of the dish. The liquid was filtered from the crystals, which were washed four times with a few drops of distilled water, and a portion removed to a cover-slip for micro-m. p. determination. Melting began at 130° and was complete at 200°. The whole of the solids were redissolved in 1—2 ml. of water, and separated into four fractions by crystallisation. The first three fractions melted at 132—136°, 132—140°, and 132—139° (triethylarsine dimercurichloride has m. p. 130—140°; Challenger and Ellis, *loc. cit.*, p. 399) and in the most soluble fraction some melting was perceptible between 136° and 142°, but a residue remained which melted at 190—198°, and may have been methyl-diethylarsine dimercurichloride (m. p. 196—198°; *idem, ibid.*).

In view of the large melting range of triethylarsine dimercurichloride, a mixed m. p. was not decisive, but a comparison between the properties of our product and those of the authentic compound left no doubt that they were identical: specimens of the latter melted at 130—140° and 132—140°, and, under the microscope, were seen to behave exactly like our product before, during, and after melting. The absence of the monomercurichloride from the product of reaction with the radicals was perplexing, but was explained when some pure monomercurichloride was recrystallised under the same conditions as in the above experiment, for the sole product was the dimercurichloride.

It is thus established that acetone on photolysis yields only methyl radicals, whereas diethyl ketone gives ethyl, with possibly a small amount of methyl. The predominance of the former is indicated by the absence of trimethylarsine mercurichlorides, which, had they been present in appreciable amounts, would have been detected by their relative insolubility in water, as shown in separate experiments.

*Photolysis of Acetaldehyde.*—Acetaldehyde at 1—2 mm. pressure was irradiated, and the products passed over cold tellurium mirrors. We confirmed the observation that the mirrors were not perceptibly affected. A considerable proportion of the acetaldehyde which collected in the liquid-air trap was polymerised, and it seemed that a small amount of this non-volatile polymeride deposited as a coherent film over the tellurium might well protect it from attack. The tube was therefore surrounded with a black paper sleeve covered (except the irradiated portion) with wet cotton-wool, and a faint tellurium mirror 3 cm. behind the arcs was subjected to the products of photolysis of acetaldehyde at 1—2 mm. for 75 mins. The mirror remained

FIG. 2.



at its original intensity. The acetaldehyde was replaced by acetone at the same pressure, but the mirror was unaltered after 15 mins.' exposure. It was clearly inactive towards methyl radicals.

The wet cotton-wool was then removed, and the mirror, still under the black paper, warmed to 80° in the heat from the arcs. It almost vanished after 10 mins.' exposure to irradiated acetone. It appeared, therefore, that an active surface could best be maintained by keeping the mirror at a temperature sufficient to prevent the deposition of a film of polymeride, and it was found that mirrors at 40°, 70°, 120°, and 150° were then attacked by photolysing acetaldehyde, the rate of removal increasing with rising temperature, whilst mirrors at 150° were unaffected by the acetaldehyde in the absence of ultra-violet light.

The character of the acetaldehyde photolysis appears, however, to change as the temperature rises, the incidence of a chain reaction becoming definite above 80° (Leermakers, *loc. cit.*), and in the experiments so far described no precautions were taken to cool the tube in the immediate vicinity of the arcs, where temperatures up to 150° were observed. A 20-cm. length of the quartz tube was therefore cooled with a shower of water (Fig. 2). Immediately behind this portion, the tube was surrounded by a closely-fitting, dull-black, paper sheath wound with nichrome wire. A small thermometer was strapped with its bulb near the position occupied by the mirror, and the whole packed with asbestos wool and kept in place by a roll of asbestos paper. The heated portion of the tube was separated from the cooled portion by a screen which effectively defined the temperature zones by preventing the creeping and splashing of water, and also restricted illumination to the cooled area. The arcs were placed on each side of the tube at A (Fig. 2). In a typical experiment, two tellurium mirrors, 1.5 mm. wide and dense enough to be dark brown, were situated 3.5 and 7.0 cm. behind the screen on its heated side and maintained at 55°. With the cooling water running, the arcs were struck, and acetaldehyde admitted at 2 mm. pressure. After 75 mins., both mirrors had disappeared. During the experiment, the quartz tube in the vicinity of the arcs remained at 17°, so that, although the radicals may have been

liberated at the mirrors by the aforementioned chain reaction, yet this must have been induced by the fragments from the acetaldehyde which was being irradiated at the room temperature.

To ascertain the nature of the radicals, a heavy tellurium mirror, 2.5 cm. long and maintained at 150°, was completely removed by the radicals from acetaldehyde, and the products separated into two fractions by distillation from a bath at -20° into liquid air. The treacly residue, consisting largely of polymerised aldehyde, was very troublesome to handle. It smelled strongly of alkyl telluride, and was pale red. On the centre tube of the condensing vessel, a drop of red, non-volatile oil was observed, which, from its properties, was evidently dimethyl ditelluride.

To compare the quantities of radicals accompanying the photolysis of acetaldehyde and acetone under identical conditions of temperature (100°), pressure (2 mm.), and irradiation, the times of disappearance of standard tellurium mirrors were compared. The experiments were carried out alternately with the aldehyde and ketone, and the mirrors prepared with the aid of the smoked standard previously described (*loc. cit.*). Acetaldehyde removed the mirrors in 150, 172, and 155 secs., mean 159; and acetone in 83, 60, 90, and 80 secs., mean 78. Hence the ratio of the quantities produced is  $159/78 = 2.07$ .

Despite some variation with wave-length, the extinction coefficient of acetaldehyde vapour (Debye, "The Structure of Molecules," London 1932, p. 122) is on the average twice as great as that of acetone (Landolt-Börnstein, "Tabellen").

The quantum yield from acetaldehyde calculated from Leermakers's data (*loc. cit.*) is 0.97 at 83° and 2.02 at 117°, giving a mean value of 1.5 at 100°, whilst the quantum yield from acetone is about unity at the same temperature (*idem, ibid.*, 1934, 56, 1899).

Therefore, at the same light intensity and pressure, since acetaldehyde absorbs twice as strongly as acetone, and the quantum yields are 1.5 and 1 respectively, the relative amounts decomposed in the same time are in the ratio  $1.5 \times 2 : 1$ . Under identical conditions, however, acetone produced 2.07 times as many radicals as acetaldehyde; hence, for equal quantities of the two compounds decomposed, there are  $1.5 \times 2 \times 2.07 = 6$  times as many radicals in the former as in the latter decomposition. It should be noted that this is of necessity an approximate evaluation, since the only data available for the calculation refer to pressures above 12 mm. and monochromatic light of wave-length 3130 Å.

#### SUMMARY.

(1) Failure to remove cold metallic mirrors with the products from photolysing acetaldehyde (J., 1934, 1718) was due to the protection of the mirrors by a film of polymerised aldehyde. Methyl radicals have now been detected by their action on warm metallic mirrors.

(2) The radicals resulting from the photolysis of acetone and diethyl ketone have been identified unambiguously as free methyl and ethyl respectively.

(3) In the photodissociation of equivalent amounts of acetone and acetaldehyde at 100° under identical conditions of pressure and irradiation, six times as many radicals participate in the former as in the latter.

(4) The results accord with those of Norrish, of Leermakers, and of Leighton and Blacet.

We are deeply indebted to Professor Challenger, of Leeds, who kindly gave us samples of trimethyl- and triethyl-arsine mercurichlorides, and suggested their use in the present work; and also to the Imperial Chemical Industries, Ltd., for a grant which assisted the purchase of apparatus.

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