53. *Free Radicals and Atoms in Primary Photochemical Processes. The Free* n-*Propyl Radical.*

By Thomas G. Pearson and Ronald H. Purcell.

Numerous attempts have been made to prepare higher homologues of methyl and ethyl. Paneth and Lautsch (*Ber.*, 1931, **64**, 2708) decomposed tetra-*n*-propyl-lead at about 400°, using the same method as had yielded free methyl and ethyl (Paneth and Hofeditz, *Ber.*, 1929, **62**, 1335), and investigated the action of the products on lead, antimony, and zinc. With lead, a yellow liquid resulted which decomposed above 100°, with separation of metallic lead and formation of minute amounts of liquid non-volatile in a vacuum at the ordinary temperature. Antimony gave bisdimethylantimony, and zinc gave dimethylzinc with traces of what may have been a higher zinc alkyl. It was assumed, therefore, that any propyl produced decomposed rapidly to give methyl. It had been observed that above 600° ethyl decomposes completely to methyl (Paneth and Loleit, J., 1935, 369), but attempts to lower the decomposition temperature of tetrapropyl lead by the use of catalysts or high-frequency discharges were unsuccessful (*idem, ibid.*, p. 380). Rice (*Trans. Faraday Soc.*, 1934, **30**, 152) sought to carry the propyl radicals in a current of ethylene in an effort to inhibit the decomposition $CH_3{\cdot}CH_2{\cdot}CH_2 \longrightarrow CH_3 + C_2H_4$, but obtained only methyl, and concluded from this and other experiments that in thermal decomposition in the range 450—750° practically all radicals higher than ethyl dissociate to give olefins and methyl, ethyl, or atomic hydrogen.

On the other hand, Rice and Evering (*J. Amer. Chem. Soc.*, 1933, **55**, 3898) passed a mixture of azo*iso*propane and acetone through a silica tube heated at 450—550°, and measured the life of active fragments in the effluent gases. The curve obtained by plotting concentration of radicals against distance from the heated zone was compared with that from tetramethyl-lead under identical conditions. The curves coincided exactly up to 20 cm.; beyond, the concentration did not diminish so rapidly with azo*iso*propane as with tetramethyl-lead, indicating the presence of an active fragment of comparatively long life.

Since methyl and ethyl had been isolated in the photodissociation of acetone and diethyl ketone respectively (Pearson and Purcell, J., 1934, 1718; 1935, 1151; Terenin, *Trans. Faraday Soc.*, 1935, **31**, 1483), it was thought that propyl should result from similar experiments with di-*n*-propyl ketone, and this expectation was encouraged by the work of Bamford and Norrish (*Chem. and Ind.*, 1935, **54**, 488; J., 1935, 1504), who, from the chemical and spectroscopic analysis of the photolysis, concluded that at least a proportion of the ketone decomposes to yield propyl radicals.

It is now shown that when di-*n*-propyl ketone is irradiated with ultra-violet light, it dissociates to form free *n*-propyl radicals. The ketone was allowed to stream at a pressure of about 2 mm. Hg through a quartz tube covered to exclude light except for a 10-cm. length which was irradiated with a quartz mercury-vapour arc. Active fragments were detected 35 cm. (the maximum available distance) from the irradiated zone by their removal of metallic mirrors. Whereas the reaction with arsenic, antimony, or tellurium might be ascribed to atomic hydrogen, that with lead precludes this possibility (Pearson, Robinson, and Stoddart, *Proc. Roy. Soc.*, 1933, **142**, 275), and limits the fragments to an organic free radical. Small quantities of the propyl derivatives of arsenic, antimony, tellurium, and lead are not readily identified. We therefore used mercury (Rice, Johnson, and Evering, *J. Amer. Chem. Soc.*, 1932, **54**, 3529; 1934, **56**, 2105), realising that the results must be interpreted with caution (J., 1935, 1151). In the present instance, we avoided exciting the mercury by irradiating with hot mercury arcs, and in subsequent experiments, as a further precaution, filtered the light through a layer of mercury vapour sufficiently thick to ensure the absence of resonance radiation. Under these conditions the products of the photolysis reacted with mercury to form an evil-smelling, colourless liquid which reacted with mercuric bromide to form crystalline plates of *n*-propylmercury bromide. No other alkylmercury bromide was revealed by the fractional sublimation of the reaction products. Hence the radical responsible for the removal of the arsenic, antimony, tellurium, and lead mirrors must have been *n*-propyl, the half-life period of which at the room temperature in a silica tube of 8-mm. diam. was found to be $2\cdot3 \times 10^{-3}$ sec., compared with $3\cdot3 \times 10^{-3}$ and $5\cdot3 \times 10^{-3}$ sec. for ethyl and methyl respectively (Paneth, Hofeditz, and Wunsch, J., 1935, 375; *Ber.*, 1929, **62**, 1335; Paneth and Lautsch, *loc. cit.*; Pearson, J., 1934, 1721).

It may be pointed out that a life period determined at the room temperature is no criterion of thermal stability, and the failure of earlier workers to obtain the propyl radical by the thermal decomposition of compounds is not irreconcilable with our results.

EXPERIMENTAL.

Di-*n*-propyl ketone (250 g.) was dried over calcium chloride, and distilled at atmospheric pressure through a 70-cm. bead column, the middle fraction (100 g.), b. p. 142—143°, being collected. Mercury was purified with nitric acid, dried, and redistilled in a vacuum. Commercially pure mercuric bromide was recrystallised from water.

FIG. 1.

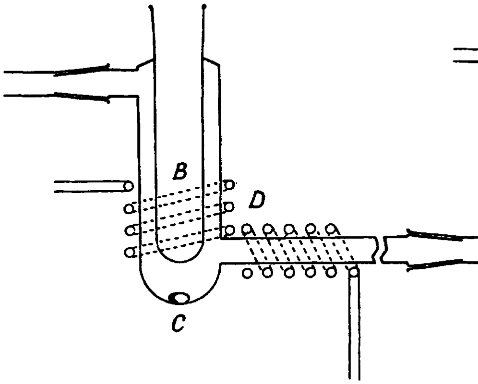
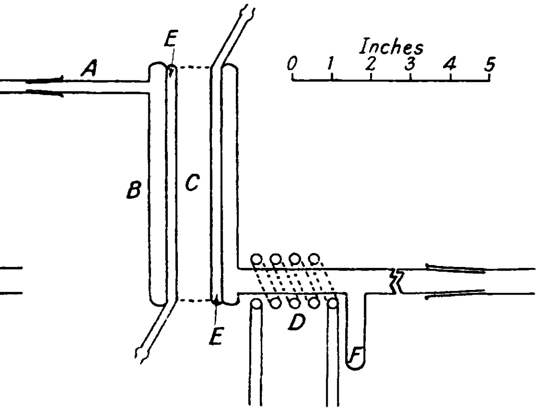


FIG. 2.



The apparatus employed for the experiments with solid metals was identical with that previously described (J., 1935, 1153). Butyl phthalate was used in the manometers to avoid the presence of mercury in the apparatus. Mirrors of arsenic, antimony, or tellurium, 2 mm. wide and dense enough to be dark brown, situated 15 cm. from the nearer edge of the irradiated zone, were removed completely in about one hour. The products condensed in the liquid-air trap were always colourless and smelled of the original ketone. The absence of the typical odour of dimethyl or diethyl telluride was noteworthy. Lead mirrors of a similar density were removed in comparable, but slightly longer, times. Mirrors were unattacked in the absence of ultra-violet light.

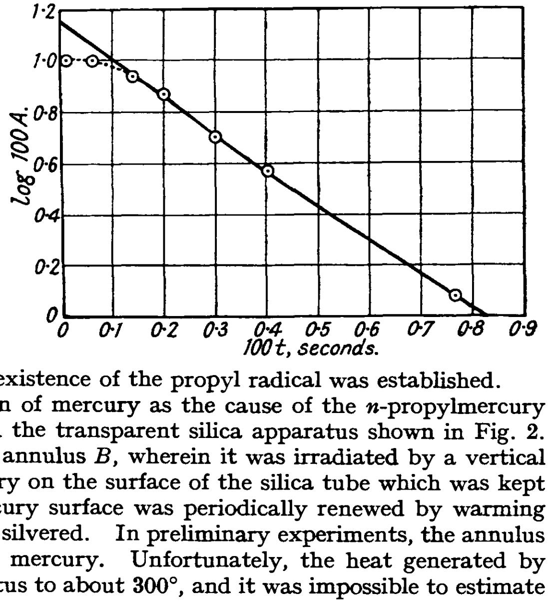
The radicals were identified by their reaction with mercury. In the earlier experiments (Fig. 1), the ketone streamed at about 2 mm. Hg through the transparent silica tube (12 mm. diam.) wherein it was irradiated by a cold arc (Thermal Syndicate, T/M5/249) and a hot arc (T/M5/254) burning on opposite sides of the tube. The products of the photolysis and excess of ketone impinged on mercury on the surface of the condenser *B*. The mercury was constantly refreshed from the pool *C* by heating with a micro-burner. In order to restrict the mercury to the immediate neighbourhood of *B*, the outside of the quartz vessel and 10 cm. of the tube were surrounded by a cooling spiral *D*. The products of the reaction with mercury and excess of ketone condensed in a liquid-air trap, and, by manipulation of taps provided in the system, could be distilled on to a small quantity of mercuric bromide with which mercury-alkyls form comparatively non-volatile alkylmercury bromides. The ketone was then re-admitted to the quartz tube, and the operations repeated. During the whole of the processes, precautions were taken to avoid the presence of mercury in the irradiated zone, and, provided it was not there to start with, the rate of streaming was sufficient to prevent diffusion against the gas stream during irradiation. Fractional sublimation of the alkylmercury bromides from four runs yielded five fractions. The first three, m. p. 136—138°, were laminated plates which began to recrystallise at 120° to form clusters of curiously curved needles, the typical appearance and behaviour of *n*-propylmercury bromide. The m. p., 136—138°, of an authentic specimen of mercuric bromide was not depressed by admixture with an equal part of the fourth fraction. The fifth fraction was the highly polarising rhombs of mercuric bromide, which sublimed from the cover-slips at 230°.

In a second experiment, the 12-mm. silica tube was replaced by one of 5-mm. diameter in order further to restrict the diffusion of mercury. To reduce the likelihood of excitation, only the hot arc was used for irradiation. All the fractions obtained melted between 136° and 138°, and from their appearance were *n*-propylmercury bromide. In an endeavour to detect other alkylmercury bromides which might have been present, the products (0·2 g.) from seven runs were collected. On sublimation, isotropic polygonal grains were obtained, m. p. 122—130°, which began at 100° to be transformed into cruciform tablets of unique appearance. This substance was unlike any individual alkylmercury bromide, or mixture of alkylmercury bromides (HgMeBr, m. p. 160—164°; HgEtBr, m. p. 193·5°; $\mathrm{HgPr^{\alpha}Br}$, m. p. 136—138°; $\mathrm{HgPr^{\beta}Br}$, m. p. 98°). It was found, however, that a mixture of mercuric bromide, *n*-propylmercury bromide, and di-*n*-propyl ketone, when evaporated to dryness and sublimed, yielded crystals that behave in an identical fashion. The same product was obtained from the first two compounds, but not from either of the others of the three possible binary mixtures. Later sublimates from the photochemical experiments melted at 136—138°, and admixture with authentic *n*-propylmercury bromide did not depress the m. p. of representative fractions.

Sublimation of the products from blank experiments in the absence of ultra-violet light yielded only mercuric bromide.

Since we had detected alkyl radicals by their action on arsenic, antimony, tellurium, and lead in the complete absence of mercury, whilst with mercury only propyl was detected, it was clear that unless the whole photodissociation had changed its course in the presence of mercury vapour—which might, in spite of the precaution, have diffused into the irradiated zone—then the existence of the propyl radical was established.

FIG. 3.



In order finally to rule out the excitation of mercury as the cause of the *n*-propylmercury bromide and to improve the yields, we used the transparent silica apparatus shown in Fig. 2. The ketone was admitted at *A* to the outer annulus *B*, wherein it was irradiated by a vertical arc in *C*, and streamed over a film of mercury on the surface of the silica tube which was kept cold by a metal water-jacket *D*. The mercury surface was periodically renewed by warming the reservoir *F*. The outer surface of *B* was silvered. In preliminary experiments, the annulus *E*, which was evacuated, contained a little mercury. Unfortunately, the heat generated by the arc raised the temperature of the apparatus to about 300°, and it was impossible to estimate how far this might influence the dissociation, so the experiment was interrupted after an hour. The products condensed in the liquid-air trap were treated with mercuric bromide and sublimed into two fractions, the second of which proved to be mercuric bromide. The first consisted of isotropic polygonal grains, which became cruciform at 100—110° and melted at 122—130°, identical with the addition compound of *n*-propylmercury bromide and mercuric bromide.

In the final experiments, we streamed cold water through the annulus *E*, and passed the lamp through accurately fitting rings which closed the inner tube and served to contain the mercury. A stream of coal-gas protected the mercury from oxidation. An asbestos screen round the lower portion of the inner mercury lamp prevented the direct irradiation of the ketone in the horizontal tube. The resonance line was absent in a photograph of the spectrum taken through a slit in the silvering. The products from five runs were treated with mercuric bromide and sublimed into fifty fractions, the earlier of which were identical with the addition compound of *n*-propylmercury bromide and di-*n*-propyl ketone, and the later gave a series of m. p.'s approaching that of pure *n*-propylmercury bromide until sublimation was interrupted on the appearance of mercuric bromide. Again, no evidence of other alkylmercury bromides was obtained. It is therefore concluded that the alkylmercury bromide did not result by the action of excited mercury atoms on the ketone, but by the action of free *n*-propyl radicals on metallic mercury.

The half-life period of the fragments, measured by comparing the rates of removal of standard mirrors in the usual way (J., 1934, 1721), was $2{\cdot}3 \times 10^{-3}$ sec. The results are shown in Fig. 3, wherein the ordinates are the logarithms of the reciprocals of the times of removal of the mirrors (A), and the abscissæ are the times (t) taken for the radicals to reach the mirrors.

SUMMARY.

The *n*-propyl radical of half-life period $2{\cdot}3 \times 10^{-3}$ sec. is formed during the photo-dissociation of di-*n*-propyl ketone in ultra-violet light, and has been detected by its action on arsenic, antimony, tellurium, and lead, and identified through conversion into *n*-propylmercury bromide with precautions to exclude the excitation of the mercury used in identification.

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