682. *Chemical Actions of Ionising Radiations on Aqueous Solutions. Part III. The Action of Neutrons and of α-Particles on Benzene.*

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The action of neutrons and of α-rays on dilute aqueous solutions of benzene has been investigated. In addition to the products (phenol, diphenyl) obtained by irradiation with *X*-rays, polyphenols and, in particular, an aliphatic dialdehyde, resulting from the opening of the benzene ring, have been isolated. The formation of these products in the case of the densely ionising radiations appears to be the result of multiple interactions on the same molecule, caused by the high local concentration of the radicals. A sensitive colour reaction of the dialdehyde can be used to indicate the action of these densely ionising radiations.

IT is well known that the total ionisation produced by ionising radiations in a solution is only partly caused by primary interaction of the radiation with molecules. When this interaction results in an ionisation, the electrons ejected from the molecule often possess a considerable amount of energy and are then capable of ionising other molecules; in fact the larger part of the total ionisation is the result of the action of these secondary electrons.

With neutrons, the primary ionisation is the result of the action of the recoil protons formed by interaction of neutrons with water molecules. Recoil protons and α-rays are charged particles possessing masses much greater than that of the electron and they produce a much denser ionisation in their tracks in the solution than do hard *X*- or γ-rays (cf. Livingston and Bethe, *Review Mod. Physics*, 1937, **9**, 245; see also the table below).

As the ions are the natural precursors of the radicals one must expect in these cases also a much higher local concentration of radicals in the tracks of the ionising particles (cf. Weiss, *Trans. Faraday Soc.*, 1947, **43**, 314; Dale, Gray, and Meredith, *Phil. Trans.*, 1949, **242**, 33).

Approximate ion densities for different radiations

[From L. H. Gray and J. Read, *Brit. J. Radiol.*, 1942, **15**, 72.]

Radiation.	Average number of ion-pairs per micron track.
γ-Rays	15
200-kv. *X*-Rays	60
Recoil protons (from 2·7-m.-ev. neutrons)	1200
α-Particles	4000

In aqueous solutions ionisation leads to the eventual formation of free hydroxyl radicals and hydrogen atoms (cf. Part I, this vol., p. 3241) thus:

$$H_2O \rightsquigarrow H + OH \qquad (1)$$

Thus, with densely-ionising radiations, the distance between like radicals is presumably of the same order as that between unlike radicals (H and OH). Consequently the likelihood of reactions of the type

$$H + H \longrightarrow H_2 \qquad (2)$$

$$OH + OH \longrightarrow H_2O + O,\ 2O = O_2 \qquad (3)$$

is greatly increased, whilst with hard *X*-rays and γ-rays, the ordinary recombination reaction

$$H + OH \longrightarrow H_2O \qquad (4)$$

generally predominates (Weiss, *Nature*, 1944, **153**, 748; *Brit. J. Radiol.*, 1947, Suppl., **1**).

Accordingly, whilst there is very little net decomposition when *X*-rays and γ-rays act on pure water freed from all dissolved substances, there is considerable decomposition on irradiation by densely-ionising radiations, and pure water, even if originally free from oxygen, will soon contain self-produced oxygen, according to reaction (3), and peroxide formation can result (Bonét-Maury, *Compt. rend.*, 1948, **226**, 1363, 1445; *Nature*, 1948, **162**, 381).

In the presence of an acceptor dissolved in the water, there is also, with neutrons or α-rays, an increased probability (compared with *X*-rays or γ-rays) of multiple action by the radicals on one and the same acceptor molecule.

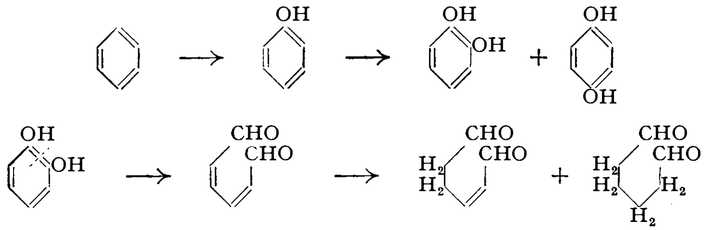
It is known that there is also a considerable difference in the biological efficiency of these two types of radiation (cf. Gray and Read, *Brit. J. Radiol.*, 1942—44; 1948, **21**, 5; Tansley, Gray, and Spear, *ibid.*, 1948, **21**, 567). However, up to the present, no more or less specific chemical reaction has been found which is given by one, but not by the other, type of radiation.

During the investigation of the action of a mixed neutron–gamma-ray source from radium–beryllium (described in detail in Part I, *loc. cit.*), it was noted that aqueous solutions of benzene, when irradiated from this source, gave a colour reaction with sulphanilic acid in slightly acid solution.

This colour reaction was traced to the presence of a small quantity of an aldehyde which could be precipitated as dinitrophenylhydrazone and is presumably an aliphatic dialdehyde (or a mixture of dialdehydes) with six carbon atoms.

At the same time quinol and pyrocatechol, in addition to phenol, were shown to be present in the solution. Similar solutions when irradiated with *X*-rays, with approximately the same total energy absorption but under otherwise similar conditions, showed no aldehyde formation.

Apparently this reaction was due to the action of the recoil protons from the neutrons present in the radium–beryllium source. In general, the phenol formed from the benzene under the influence of the radiation must become an acceptor, and when accumulated in sufficient quantities will be attacked further, yielding polyphenols. If pyrocatechol is formed thus, a further attack on this may well result in the opening of the benzene ring according to the scheme :



It is of some interest that the metabolism of benzene in the organism is somewhat similar, as it yields, not only phenol and polyphenols (see, *e.g.*, Baernstein, *J. Biol. Chem.*, 1945, **161**, 685), but also muconic acid (see, *e.g.*, Bernhard and Gressly, *Helv. Chim. Acta*, 1941, **24**, 83). Whilst therefore the formation of aldehydic substances under the influence of *X*-rays and γ-rays cannot be completely excluded at very high doses, with neutrons much smaller energies are sufficient to produce some of these products. This can be attributed to the denser ionisation in this case and to the production of hydroxyl radicals in such spatial proximity that multiple attacks on the same molecule become more likely. To substantiate this, experiments were carried out with radon, giving a nearly pure α-radiation. The experimental details have already been given (Part I, *loc. cit.*). Here too, it could be shown that an aldehyde was formed.

The dinitrophenylhydrazone of the dialdehyde gives an intense violet colour in alkaline solution and this has been used as a qualitative test for the presence of the aldehyde.

We hope to be able, in the near future, to carry out quantitative experiments, using a pure neutron source, to show whether this reaction can be used for the determination of doses of more densely ionising radiations, and to accumulate larger quantities of the aldehyde for its definite identification.

Benzoic acid in dilute aqueous solution similarly gives this colour reaction, indicating the formation of an aldehyde. This latter reaction has not yet been investigated in detail.

EXPERIMENTAL.

The irradiation vessels and the radiation sources have been described in Part I (*loc. cit.*). Saturated solutions of benzene, as described in Part II (preceding paper), were used. Analysis of the irradiated solutions, and identification of the phenolic compounds, were carried out according to the procedure described in Part II. The formation of diphenyl in small quantities has been observed also in the present experiments.

Isolation of the Aldehyde.—Solutions irradiated with the neutron–gamma-ray source were concentrated at room temperature in a vacuum. Several residues were united and slightly acidified with dilute sulphuric acid, and a solution of dinitrophenylhydrazine (2·5 mg./ml. in 2N-sulphuric acid) was added. The precipitate was filtered off, dissolved in light petroleum (b. p. 40—60°), and chromatographed on alumina. A purified specimen melted at 136° (uncorr.) (Found, by Drs. Weiler and Strauss, Oxford: C, 45·1; H, 4·0; N, 23·5. Calc. for $C_{18}H_{14}O_8N_8$: C, 45·9; H, 3; N, 23·8. Calc. for $C_{18}H_{18}O_8N_8$: C, 45·5; H, 3·8; N, 23·6%). The analytical figures do not exclude the possibility of a mixture of muconic dialdehyde with its partly or fully hydrogenated derivatives.

Colour Test for the Presence of the Aldehyde.—To the irradiated solution, or to an aliquot part thereof, 5 ml. of the dinitrophenylhydrazine solution (see above) were added. After 15 minutes the solution was extracted with carbon tetrachloride, and the extract washed with dilute sulphuric acid and then shaken with 2N-sodium hydroxide. The colour thus formed is stable for some hours. The colour formed when an acid solution of sulphanilic acid is added to the irradiated solution is stronger but transient, fading in 1—2 minutes.

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