Chemical Effects of Ionizing Radiations

IN 1944 it was suggested[1] that the primary net process in the action of penetrating radiations (γ-rays, X-rays, etc.) on the water molecule consists in its splitting in the following way :

$$H_2O \rightarrow OH + H,$$

which presumably takes place by way of the formation of H_2O^+ and H_2O^-. All the known chemical effects in aqueous solutions can be interpreted on this basis[1,2], which furthermore permits an adequate description of the biological effects of radiations[3,4]. Recently, Dainton[5] found that acrylonitrile in dilute aqueous solution on irradiation by X-rays or γ-rays shows polymerization, which he attributed to the action of primarily formed hydroxyl radicals (according to the above scheme) in view of the fact that these radicals are known to initiate polymerizations[6].

We have now succeeded in demonstrating the mode of action of penetrating radiations in aqueous solutions by investigating the reaction products formed by irradiating some simple organic substances such as benzene and benzoic acid in dilute aqueous systems. If hydroxyl radicals are formed primarily, it should be possible to isolate some of the corresponding substances containing OH groups, that is, products of hydroxylation. This, indeed, proved to be the case.

Benzene, suspended in water from which oxygen had been carefully excluded, was irradiated by X-rays by bringing it close to the target of a 200-kV. tube, and a dose of the order of 10^6 r. units was given. This resulted in about 0·1 millimol. of phenol being formed, which was identified as the tribromo derivative. A number of other substances were also found in smaller quantities, among which diphenyl was isolated.

In the irradiation of dilute aqueous solutions of benzoic acid by X-rays, under similar conditions, approximately 0·1 millimol. of hydroxybenzoic acids were formed. Salicylic acid was isolated and was identified by colour reactions and as p-nitrobenzene-azo-salicylic acid[7]. (The X-ray irradiations were carried out at the Royal Victoria Infirmary, Newcastle-upon-Tyne ; we are indebted to Dr. F. T. Farmer, who made all the quantitative determinations of the X-ray dosage.)

We have also carried out similar experiments using a neutron–γ-ray source (corresponding to 1 gm. of radium mixed with beryllium powder). With this source, benzene gave, in addition to the products mentioned above, catechol and products originating from the opening of the benzene ring. This difference is presumably due to the higher local concentration of radical produced by the recoil protons (from the neutrons).

In all these cases the total yield of the hydroxylated reaction products depends on the pH of the solutions.

The above results suggest the following sequence of reactions in the case of benzene and benzoic acid :
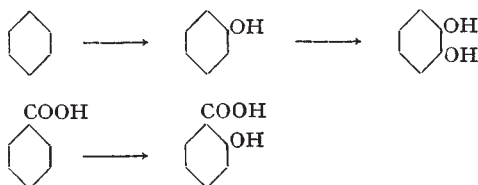
In the case of benzene, the intermediate formation of free phenyl radicals is suggested by the appearance of small amounts of diphenyl among the reaction products. The dehydrogenation to the phenyl radical may be due to a reaction with the hydroxyl radical or possibly with hydrogen atoms. Experiments to decide this are in progress.

The results indicate that : (i) Hydroxyl radicals are formed by the action of radiations on aqueous systems, since the reaction products found are the same as those obtained by the action of hydroxyl radicals produced chemically (for example, by the system $H_2O_2 - Fe^{II}$ salt). (ii) The oxidation products are very similar to those obtained in the biological oxidation of these substances, which suggests that hydroxyl radicals may play an important part in certain biological oxidations[8].

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A full account of this work will be published elsewhere.

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[1] Weiss, J., Nature, 153, 748 (1944).
[2] Cf. Lea, E. D., "Actions of Radiations on Living Cells", 47 (Cambridge University Press, 1946).
[3] Weiss, J., Nature, 157, 584 (1946).
[4] Weiss, J., Trans. Farad. Soc., 43, 314 (1947).
[5] Dainton, F. S., Nature, 160, 268 (1947).
[6] Cf. Evans, M. G., et al., Trans. Farad. Soc., 42, 668, 675 (1946).
[7] Cf. Beilstein, 4th ed., 16, 247.
[8] Cf. Haber, F., and Willstätter, R., Ber., 64, 2844 (1931).

A Coefficient of Viscous Extension

WHILE working on a generalized theory on straining of amorphous or quasi-amorphous solids, it became clear that one could include the straining of viscous fluids by means of a suitable stress-strain parameter λ which I call a 'coefficient of viscous extension' related to the 'coefficient of viscous shear' usually called[1] the coefficient of viscosity μ. In this communication only the flow strain component of a deformed substance[2] is considered, so that the elastic and plastic components[3] are neglected and, further, only isotropic substances are discussed.

An infinitesimal angle γ_{ij} of shear 'slide' has twice the arithmetical value of the normal strain e_{ij} in the 'auxiliary' plane at 45° to the planes on which the shear stress S_{ij} operates[3,4]. Hence, differentiating with respect to time t and using the coefficient of viscosity gives

$$2 \frac{\partial e_{ij}}{\partial t} = \frac{\partial \gamma_{ij}}{\partial t} = \frac{S_{ij}}{\mu}. \tag{1}$$

But the normal strain e_{ij} due to shear can be regarded as due to the 'partial' strains ε_{ij}, ε_{ji} and transverse contraction ratio q[5,1,2,3]. But the partial strain ε_{ji} is equal to but of opposite sign to ε_{ij}, so that

$$e_{ij} = (1 + q)\varepsilon_{ij}. \tag{2}$$

The normal stress T_{ij} is 'auxiliary' to, and of the same arithmetical value as, the shear stress S_{ij} if the