680. *Chemical Actions of Ionising Radiations on Aqueous Solutions. Part I. Introductory Remarks and Description of Irradiation Arrangements.*

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The development of the theory of the action of ionising radiations on aqueous solutions, leading up to the theory of formation of free radicals (Weiss, *Nature*, 1944, **153**, 748), is discussed. Apart from the intrinsic interest in the action of the radiations, these investigations are of interest because they allow the reactions of free radicals to be studied in the absence of interfering reagents and because the products of reaction are somewhat similar to those obtained in biological systems in which the same molecules are involved.

Experimental arrangements for irradiations with (i) *X*-rays (γ-rays), (ii) neutrons, and (iii) α-rays, used in the following investigations and the radiation dosimetry, are discussed in detail.

THE action of ionising radiations has been studied for many years mainly from the points of view of the physicist and the biologist. The interest of the former lies in energy-transfer processes; gaseous systems and, to some extent, solids were the main subjects of his research, while liquids and especially solutions were hardly investigated. Formally the biologist deals with aqueous systems, but his real interest lies in the action on highly organised systems—so highly organised that their formal similarity with aqueous solutions should not be unduly emphasised. It has become clear, however, in recent years that for a fundamental understanding of the biological action of ionising radiations it is necessary to study the underlying chemical processes. Consequently the investigation of simple systems in aqueous solutions is of prime interest.

From the accumulated physical, biological, and chemical evidence (cf. Allsopp, *Trans. Faraday Soc.*, 1944, **40**, 79; Lea, " Actions of Radiations on Living Cells," 1946; Lind, " Chemical Actions of Alpha Particles and Electrons," 1928) two theories of the mode of action of ionising radiations emerge : (i) the target theory, and (ii) the theory of indirect action.

The target theory grew out of the biological work, based on investigations of significant biological changes (lethal effects, mutations, etc.) in complex systems. It postulates an active " hit " by the incident radiation within a well-defined target area.

In recent years, however, evidence has become increasingly available that, whilst direct " hits " may be responsible for some specific biological effects, many biological and chemical actions are caused by indirect effects, in which the solvent medium plays a decisive part. Thus, quantitative experiments mainly due to Fricke (cf. *J. Chem. Physics*, 1938, **6**, 229) and Dale (cf. *Brit. J. Radiol.*, 1943, **16**, 171; 1947, Suppl. 1) have shown that, with ionising radiations, not only the quanta absorbed by the substrate itself but also the very much greater part absorbed by the bulk of the solvent (*i.e.*, water) react in some indirect way on the dissolved substance.

Risse and Glocker (*Z. Physik*, 1928, **48**, 845; *Z. physikal. Chem.*, 1929, *A*, **140**, 133) were the first to show that in the decomposition of hydrogen peroxide by *X*-rays the amount of chemical change is proportional to the total radiation energy absorbed, and nearly independent of the concentration of the substrate as well as of the wave-length of the radiation. Fricke, in a series of investigations (*loc. cit.*), showed that these results can be interpreted by an indirect action involving some intermediate which he termed " activated water." Dale (*loc. cit.*), in a series of elegant experiments of a more biological character (in which use was made of the deactivation of enzymes), has pointed out the significance of this independence of the concentration, which he called " dilution effect."

In recent years the interest in the action of ionising radiations has increased. The review of the situation by Allsopp (*loc. cit.*) stimulated an attempt to develop a theory which was designed to bring radiation chemistry into line with the general chemical behaviour of aqueous solutions (Weiss, *Nature*, 1944, **153**, 748; 1946, **157**, 584; *Trans. Faraday Soc.*, 1947, **43**, 314; *Brit. J. Radiol.*, 1947, Suppl. 1, 56).

Although a certain parallelism exists between radiation chemistry and ordinary photochemistry, there is first of all the important difference that, whilst in photochemistry the absorption of the radiation is specifically connected with a particular group or bond, the absorption of ionising radiations is practically independent of the chemical bonding and depends mainly on the mass of the absorber, absorption occurring throughout its volume. Consequently, in dilute solutions most of the radiation energy is absorbed by the solvent medium where the greater number of primary changes must take place.

It is well known that the absorption of ionising radiations generally results in *excitation* and *ionisation*. When the solvent is water the following electron-transfer processes are likely to be of importance :

$$H^+ \cdots OH^- + \text{radiation} \longrightarrow H + OH \quad . . . . \quad (1)$$

$$(H_2O \cdots H_2O) + \text{radiation} \longrightarrow (H_2O^+ \cdots H_2O^-) \quad . . . . . . \quad (2)$$

followed by :

$$H_2O^+ \rightleftarrows H^+ + OH \quad . . . . \quad (2a)$$

$$H_2O^- \rightleftarrows OH^- + H \quad . . . . \quad (2b)$$

All these processes are energetically possible and supported independently by photochemical evidence (cf. Weiss, *loc. cit.*). One obtains therefore ultimately hydroxyl radicals and hydrogen atoms, the initial distribution of which should correspond to that of the positive and negative ions respectively (cf. Lea, *Brit. J. Radiol.*, 1947, Suppl. 1; Weiss, *loc. cit.*).

In general one may assume that the concentration of the radicals or atoms (OH and H) is proportional to that of their ionic precursors.

There is, however, a second feature, which is characteristic of ionising radiations and absent in photochemical reactions, namely the fact that the ions (radicals) are actually produced in the tracks of the ionising particles as a result of the columnar ionisation. It is for this reason mainly that the recombination reaction

$$H + OH \longrightarrow H_2O \quad . . . . \quad (3)$$

which will depend on the *local* concentration of the radicals, varies with the nature and wavelength of the primary radiation.

In general, hydroxyl radicals and hydrogen atoms are the reacting species and one would therefore expect oxidation and reduction processes to result from the chemical action of ionising radiations. This is in agreement with the facts. There exists, however, also the possibility of some reactions of the unstable ionic species in the equilibria (2*a*) and (2*b*).

The theory as presented in the papers cited above is capable of giving a qualitative and quantitative explanation of most of the known experimental facts (cf. Allsopp, *Brit. J. Radiol.*, 1947, Suppl. 1; Dainton, *Nature*, 1947, **160**, 268).

It was desirable to furnish further and more direct chemical evidence for the nature of the intermediates involved. Preliminary reports of some of these results were published some time ago (Stein and Weiss, *Nature*, 1948, **161**, 650; **162**, 184). The following papers record the detailed results and some further work.

In addition, the investigation of the action of ionising radiations is of interest because, as is shown in the following papers, (i) it allows the study of the action of free radicals on other molecules in the absence of interfering reagents, and (ii) we have found that the products of reaction are somewhat similar to those obtained in biological reactions in which the same molecules are involved.

Experimental Arrangements for Irradiations.—In some of the present experiments particular attention was given to the actual isolation of the irradiation products, so that the evidence for our interpretations might be in the most convincing form. This led at once to the need for very large doses of radiation compared with those normally required for biological experiments, and consequently to a certain difficulty in technique. In biological irradiations it is easy to see that only very small amounts of chemical products can be formed, and it is probable that the effects achieved are due either to the extreme sensitivity of the organism to the radiation, or to some action of the radiation on the enzyme systems.

Physical Radiation Dosimetry.—The yield of a compound formed in a solution through which radiation is passed depends on the amount of energy absorbed. The latter is customarily measured in röntgens. This unit, by definition, relates to the energy absorbed in an air cavity in the liquid, surrounded by an air-equivalent wall, and not directly to the energy absorbed in the liquid itself. These two amounts of energy are closely related, but it is necessary to distinguish between them.

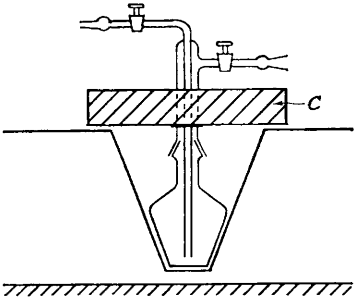
The absorption of 1 röntgen corresponds to the liberation of 1 e.s.u. of charge per ml. of air, which is equivalent to the production of $1{\cdot}61 \times 10^{12}$ ion pairs per g. of air. It is known that the average energy absorbed in the production of one ion pair in air is approximately 32·5 ev., so that 1 röntgen corresponds to the absorption of $52{\cdot}4 \times 10^{12}$ ev., or about 85 ergs per g.

It is not known with certainty how much energy is absorbed in the production of one ion pair in water, but there are reasons to believe that it is not very different from that in air. The absorption coefficients, however, for radiation in the two media are different, and the number of ion pairs produced in water by the absorption of 1 röntgen is not, therefore, the same as in air, and depends on the wavelength of the radiation used. Expressed as energy absorption per röntgen, the value varies from about 83 ergs per g. for soft X-rays to about 93 for hard X-rays or γ-rays.

In radiation-chemistry experiments it is clear, therefore, that the röntgen is not an ideal unit, and that one expressing the total energy absorbed per unit mass of liquid is much to be preferred. Gray and Read's energy unit (*Brit. J. Radiol.*, 1940, **13**, 371) was introduced for this reason. Their unit is defined as the amount of radiation contributing the same energy absorption per unit mass of material as 1 r. of γ-rays gives to an equal mass of water. The two units, röntgens and energy units, are numerically equal for hard radiations, similar to γ-rays, but differ by amounts of up to 10% for softer radiations. We shall denote Gray and Read's unit by E.U.; then, as nearly as is known, 1 E.U. corresponds to an energy absorption of 93·1 ergs per g. of water.

Fig. 1.

Schematic representation of the irradiation arrangement for X-*rays.*



C, *ionisation chamber.*

The chemical (ionic) yield due to a given amount of radiation may be calculated if the number of molecular conversions per ion pair is known. For a tentative estimate it may be supposed that each ion pair results in one molecule of product being formed. It may be seen then that the chemical yield from doses of the order of a few hundred röntgens, as used in biological experiments, cannot be more than about 10^{-9} mole per ml. of solution, an amount which does not generally admit the use of ordinary microchemical methods. If yields of the order of 0·1 millimole of substance are to be obtained, in a volume of, say, 100 ml., doses of the order of 10^6 röntgens are required. The design of ordinary X-ray equipment does not in general lend itself to the giving of doses of this magnitude.

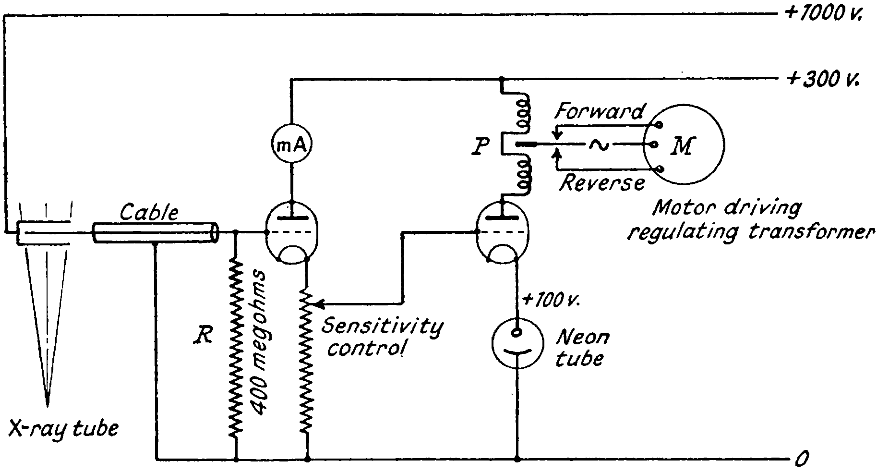
X-*Ray Irradiations.*—In order to provide this necessary dosage, a special glass vessel was constructed to fit in close proximity to the target of a 200-kv. X-ray tube (Victor Maximar). The target was cooled with circulating oil and allowed a continuous heat dissipation of 3 kw., and the vessel, placed in the displacement cone, came within about 1 cm. of the tube-wall where the dose rate was of the order of 3500 r./min. The general arrangement for irradiations is shown in Fig. 1.

Continuous irradiations up to 10 hours were made to give the necessary doses. In order to keep the tube output constant for this interval a special stabiliser was employed (Clayton and Farmer, *Brit. J. Radiol.*, 1949, **22**, 669). This included an ionisation chamber (C), placed in the X-ray beam, the saturation current from which was amplified and caused to operate a motor driving a voltage-regulating transformer. The transformer controlled the incoming mains voltage to the set. Thus, if the output tended to rise, the ionisation current increased and the motor ran in a direction to reduce the incoming voltage, and *vice versa*; the output was thereby maintained constant within, on the average, 2—3% over long periods. The schematic arrangement of the stabiliser is shown in Fig. 2.

The integral dose in the flask was determined by taking a series of readings of dose at different points in the liquid, using a condenser-ionisation chamber of very small air volume and large capacity (Farmer, *Brit. J. Radiol.*, 1945, **18**, 148). Since the radiation field was inhomogeneous, falling off rapidly with distance from the bottom of the flask, iso-dose curves were plotted in the contour of the vessel, and from these the effective dose to the solution was determined by graphical integration (Fig. 3). The value thus obtained for the mean dose rate was 3600 r./min. or about 3300 E.U./min.

FIG. 2.

Diagrammatic representation of the output stabiliser.

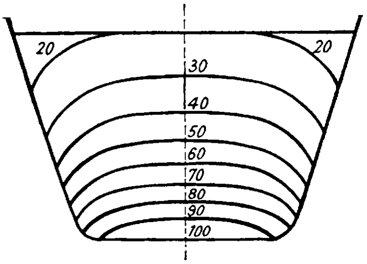


The ionisation current flowing through R *controls the polarised relay* P, *and thereby actuates the motor* M, *which is coupled to the input-regulating transformer.*

Later, some of the reactions employed during the course of the work were found to have a useful application in the chemical measurement of radiation dosage (Day and Stein, *Nature*, 1949, **164**, 671), and use was made of this to check the integral dose in the flask by comparing it with effects in a small (1-ml.) specimen irradiated with a known dose of X-rays. The value obtained by this second method was 3320 E.U./min., in good agreement with the previous value.

FIG. 3.

Radiation field in the reaction vessel.



Iso-dose curves.

The radiation from the X-ray tube was filtered only by the glass wall of the tube and other light materials, and therefore had a very broad spectral distribution. The equivalent monochromatic wave-length, as determined from absorption measurements in copper, was about 0·17 A.

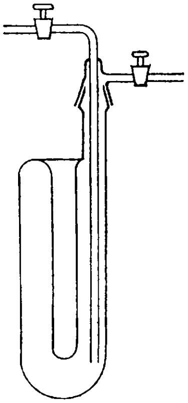
In addition to those with X-rays, some measurements were made with γ-rays from radium, using a simple arrangement of platinum tubes containing in all about 1·2 g. of radium.

Neutron Irradiations.—A neutron source consisting of radium–beryllium was used, irradiations with this being carried out at the Londonderry Laboratories for Radiochemistry at Durham. We are greatly indebted to Professor F. A. Paneth for providing this facility. The source gave a mixed neutron–γ-ray radiation, consisting of approximately $1·5 \times 10^7$ neutrons per second and $3·7 \times 10^{10}$ γ-ray quanta per second. These irradiations were carried out in the vessel shown in Fig. 4, the source being inserted into the central cavity, surrounded by the irradiated solution. The time of the irradiation in this case was of the order of two weeks.

α-*Ray Irradiations.*—The source of α-rays used was radon. For these experiments the vessel shown in Fig. 5 was employed. A radon capillary was introduced first, the test solution added, and the vessel closed by inserting the ground-in stopper. By turning this latter, the capillary was then crushed, and the radon escaped into the solution. The duration of irradiations was again of the order of two weeks, the total dose being determined by the decay of radon. The total radon employed was about 10 mc. per experiment. The amount of radon in the each capillary was estimated previously by γ-ray measurement with an ionisation chamber and a standard radium tube.

FIG. 4.

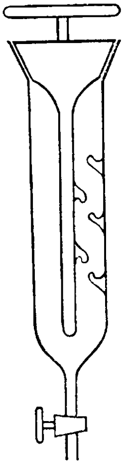
Schematic representation of the vessel used for the neutron irradiations (scale approx. $\frac{1}{8}$*).*



The Ra–Be *source is inserted in the central cavity which is surrounded by the solution.*

FIG. 5.

Schematic representation of the vessel used for the experiments with α-rays (scale approx. $\frac{1}{2}$*).*



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