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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

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Yields of Water Radiolysis Products in Acid Solutions Saturated with Argon under High Pressure

(Presented by Academician A. N. Frumkin, February 23, 1965)

In radiation chemistry, up to the present time no attention has been paid to the study of the question of the influence of the structure of water on the processes that occur during its radiolysis. Meanwhile, it is known that the yields of radiolysis products change noticeably on going from the liquid phase to the solid phase, and in the latter—from whether the sample is irradiated in the crystalline or glassy state (^1). One of us had earlier (^2) put forward the supposition of a probable role of the microstructure of water, determined by hydrogen bonds, in the radiolysis process.

Fig. 1. Dependence of the yield of oxidation of ferrous ion on the gas pressure above the solution. 1—argon, 2—helium, 3—nitrogen

Fig. 2. Accumulation of radiolysis products as a function of dose. 1—Fe^3+; 2—Ce^3+; 3—H_2O_2

To clarify the role of the structure and of its destruction in liquid water in the processes occurring during radiolysis, solutions of Fe^2+ in the presence of oxygen, $Ce(SO_4)_2$, and a mixture of $H_2 + O_2$ in 0.8 N H_2SO_4, saturated with argon under pressures up to 2800 atm, were subjected to irradiation. Under these conditions the structure of water may undergo a substantial change owing to the destruction of hydrogen bonds at pressures of 1500 atm (^3) and in connection with the introduction of noble-gas atoms, the concentration of which reaches 1-1.5 M, into the intermolecular voids, which also leads to destruction of the water structure existing under ordinary conditions. It was found that upon a gradual increase of the gas pressure from 1 to 100 atm no change in the yields is observed. In the region from 100 to 1500 atm a considerable increase in the yields is observed, which, upon a further increase of pressure to 2800 atm, no longer change (Fig. 1). The accumulation of radiolysis products with dose for solutions saturated with argon at 2000 atm is shown in Fig. 1. The yields

calculated from these data are: $G(Fe^{3+})_{O2} = 29$ ions/100 eV, $G(Ce^{3+}) = 10.0$ ions/100 eV, $G(H_2O_2)_{H_2+O_2} = 9.6$ molecules/100 eV. All these values are substantially higher than the values found under ordinary conditions. The results obtained in these three syste-

The data allow one to calculate the yields of radicals and molecular products and the observed yield of water decomposition. Indeed, in accordance with the generally accepted schemes:

$$G(Fe^{3+})_{O2} = 3G_H + G_{OH} + 2G_{H_2O_2} = 4G_H + 2G_{H_2} = 29;$$

$$G(Ce^{3+}) = G_H - G_{OH} + 2G_{H_2O_2} = 10.0;$$

$$G(H_2O_2)_{H_2+O_2} = \tfrac{1}{2}(G_H + G_{OH}) + G_{H_2O_2} = 9.6.$$

From this we find: $G_H = 4.9$; $G_{OH} = 4.6$; $G_{H_2} = 4.7$; $G_{H_2O_2} = 4.85$. The total observed yield of water decomposition is then equal to 14.3 mol/100 eV. This value is apparently too large to be explained solely by ionization processes: an essential role must be assigned to excitation processes. Noteworthy is the sharp increase in the yields of molecular products. If it is a consequence of the effective realization of excited states under these conditions, then this fact casts doubt on the substantial role of track formations which has hitherto been assigned to them in the case of light radiations. Of course, this assumption must also be checked by other methods, for example by the effect of changing the acceptor concentration on the yield of molecular products.

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Note: Figure translations are in progress. See original paper for figures.