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Abstract

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STATIONARY STATES IN THE RADIOLYSIS OF NEUTRAL AQUEOUS SOLUTIONS OF OXYGEN

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During prolonged irradiation of solutions of oxygen in water, the establishment of a stationary state is observed for the molecular products of radiolysis—hydrogen, oxygen, and hydrogen peroxide. The onset of such a state is due to the fact that the stable products of radiolysis, accumulating in sufficient concentrations, begin to interact with radicals formed under the action of radiation and themselves are thereby destroyed. Since the onset of this state, which is a dynamic equilibrium, is caused by the competition of a whole series of reactions, in the general case depending in different ways on such factors as the concentration of the introduced acceptor, pH, dose rate, and temperature, one may expect that analysis of the influence of these factors on the stationary state will make it possible to clarify the probable mechanism of the process and to determine the quantitative characteristics of the competing reactions.

According to data available in the literature, the stationary concentrations of the molecular products of radiolysis depend strongly on the concentration of oxygen dissolved in water (^{1}). For pure water the stationary concentrations of H_2 and H_2O_2 have very small values (of the order of 10^{-5}–10^{-6} M for X-radiation, γ-radiation, and electrons). In the presence of oxygen the stationary concentrations of H_2 and H_2O_2 increase, and the stationary state itself is reached at considerably larger doses than in the case of pure water (^{2}). Starting from the assumption of two types of reducing particle and the accepted mechanism of radiolysis for a system containing hydrogen peroxide, hydrogen, and oxygen, it was shown theoretically that the stationary concentrations of the molecular products of radiolysis should not depend on the dose rate, while the ratio $[O_2]_{st}/[H_2O_2]_{st}$ is equal to a constant value and does not depend on the absolute values of the concentrations of hydrogen peroxide and oxygen (^{3}). In a theoretical consideration of a general model of water radiolysis, it turned out that the logarithms of the stationary concentrations of any molecular products of radiolysis, when the dose rate changes from I_1 to I_2, should change by the amount $\lg(I_1/I_2)^{1/2}$. Such a regularity is a consequence of the uniform distribution of radiolysis products over the volume of the solution and of the occurrence between them of only bimolecular reactions. Fulfillment of the indicated regularity, on the other hand, is a strict criterion for the conditions formulated above for the course of the radiation-chemical process (^{4}).

Experimental work whose results could be used to test the indicated theories was carried out over a very limited range of dose rates of X- and γ-radiation. It was of interest to compare the theoretical and experimental dependence of the stationary concentrations of H_2, H_2O_2, and O_2 on dose rate over a broader range.

Irradiation of solutions of oxygen in water was carried out with a γCo^{60} source (40,000 g-equiv. radium) in cells equipped with mercury manometers. The ratio of gas and liquid volumes in all experiments was 0.25–0.33.

The cells containing the solution were shaken continuously during irradiation. This achieved an equilibrium distribution of oxygen and hydrogen between the volumes of liquid and gas, necessary for attaining the stationary state. After irradiation, the change in the total pressure of the gases above the solution and the concentration of hydrogen peroxide were measured. The latter was determined by a spectrophotometric method. The concentrations of hydrogen and oxygen were calculated from data on the change in gas pressure at the beginning and at the end of the experiment, taking into account the stoichiometric relationships between the initial and final products in this system (H_2O, O_2, H_2O, and H_2). The dose rate was determined using a Fricke dosimeter ($G(Fe^{3+}) = 15.6$).

[Fig. 1 and Fig. 2: plots of stationary concentrations versus dose-rate functions.]

Fig. 1. Dependence of the stationary concentration of hydrogen peroxide on the square root of the dose rate.
1 —initial oxygen concentration $1.4 \cdot 10^{-3}$ mol/l, **2** —initial oxygen concentration $2.8 \cdot 10^{-4}$ mol/l.

Fig. 2. Dependence of the stationary concentration of hydrogen on the square root of the dose rate. The notation is the same.

The dependence of the hydrogen peroxide concentration and of the total gas pressure above the solution on dose showed that the stationary state is reached at a dose of the order of $5 \cdot 10^{19}$ eV/ml over the entire interval of dose rates studied. Since all experiments were carried out at a total dose of the order of 10^{21} eV/ml, attainment of the stationary state was always ensured. Figure 1 shows the change in the stationary concentration of hydrogen peroxide as a function of the square root of the dose rate for two different initial oxygen concentrations: $2.8 \cdot 10^{-4}$ mol/l (curve **1**) and $1.4 \cdot 10^{-3}$ mol/l (curve **2**). Figure 2 gives the analogous dependence for the stationary concentration of hydrogen. In these figures two regions of dependence of the stationary concentrations of hydrogen peroxide and hydrogen on $\sqrt{I}$ are clearly visible. The first is a region of linear dependence on the square root of the dose rate, and the second is

Fig. 3 and Fig. 4

Figure 1: Fig. 3 and Fig. 4

nonlinear. In the case of hydrogen peroxide, we observe the attainment of a certain limiting value at a definite dose rate and a subsequent independence of the stationary concentration of hydrogen peroxide from the dose rate. This is apparently connected with a different mechanism of water radiolysis in different intervals of dose rate. In the case of hydrogen, after attainment of a certain value of the stationary concentration at a definite dose rate, a slight decrease in it is observed. Such a decrease may apparently be connected with the appearance, at increased dose rates, of an oxidizing species different from the OH radical, which reacts effectively with molecular hydrogen. The stationary oxygen concentration is practically independent of the dose rate.

Figure 3 shows the dependence of the ratio $[\mathrm{O_2}]_{\mathrm{st}}/[\mathrm{H_2O_2}]_{\mathrm{st}}$ on the square root of the dose rate. At low dose rates

dose is some function of its value, which is in contradiction with the conclusion drawn by Allen (^{3}). At increased dose rates the value of the ratio reaches a limit equal to 1.85 at an initial oxygen concentration of $2.8 \cdot 10^{-4}$ mole/l and 2.75 at an initial oxygen concentration of $1.4 \cdot 10^{-3}$ mole/l. This dependence of $[O_2]_{\mathrm{st}}/[H_2O_2]_{\mathrm{st}}$ on $\sqrt{I}$ also indicates that, apparently, different mechanisms of radiolysis are possible in different dose-rate intervals.

Figure 4 shows curves of the dependence of the stationary concentrations of hydrogen peroxide and hydrogen on the concentration of oxygen and on the dose rate,

Fig. 3. Dependence of the ratio $[O_2]_{\mathrm{st}}/[H_2O_2]_{\mathrm{st}}$ on the square root of the dose rate. The designations are the same.

Fig. 4. Dependence of the stationary concentrations of hydrogen peroxide and hydrogen on the stationary concentration of oxygen. The designations are the same.

constructed by the method proposed by Ershler (^{4}). In this figure are plotted experimental data in which the stationary concentrations of hydrogen and hydrogen peroxide were determined for five different initial oxygen concentrations (solid points) at $I = 2.95 \cdot 10^6$ eV/ml • sec. The remaining points were plotted by shifting the origin of coordinates along the intensity axis, using the data presented in Figs. 1 and 2. All the points fell on one curve, close to that which was theoretically calculated by Ershler. This fact allows us to conclude that the assumption of a uniform distribution of radiolysis products throughout the volume should be considered correct.

Further investigations are aimed at clarifying the dependences which, as we hope, will help substantiate the mechanism of the reactions occurring in this system.

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CITED LITERATURE

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