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Abstract

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ON THE DEPENDENCE OF THE YIELD OF RADIATION-CHEMICAL REACTIONS ON THE CONCENTRATION OF DISSOLVED SUBSTANCES

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The mechanism by which many radiation-chemical transformations proceed is often established on the basis of experiments performed upon irradiation of a solution of some single concentration. Usually the choice of this concentration is accidental, and a number of authors, in order to obtain comparable data, use identical concentrations of the irradiated solutions. Sometimes a certain small range of concentrations is investigated, and the experiments are broken off without a thorough study of the concentration dependence of the transformation yield. It is readily found, however, that a large change in the concentrations of dissolved substances leads to a sharp change in radiation-chemical yields. The observed effects do not fit within the framework of a mechanism previously thought quite acceptable for explaining the nature of processes occurring in solutions of intermediate concentrations. Such processes include, for example, the reactions observed in aqueous solutions of radiolytic oxidation of ferrous ions, reduction of nitrate ions, ferric ions, and others.

It is obvious that each free radical formed in the radiolysis of a medium (for example, water in aqueous solutions) can react with another—or with a similar—radical, or with a molecule of the dissolved substance (acceptor), with a probability proportional to their concentration and to the cross section of the reaction of such an interaction. The concentration of the radicals initially formed along the track falls very rapidly and, apparently, can be calculated exactly only with the use of computing machines. However, using elementary ideas of a track model, by means of very approximate methods of graphical integration, one can calculate the average concentration of free radicals in a track at which a definite fraction of all the radicals formed disappears. Thus, using Gray' s model (^1), the author came to the conclusion that the first quarter of all the radicals formed (for β-particles, accelerated or secondary electrons) reacts at an average concentration $C_1 = 1.5 \cdot 10^{-5}$ M, the second quarter at $C_2 = 3 \cdot 10^{-6}$ M, the third at $C_3 = 5 \cdot 10^{-7}$ M, and the last quarter at $C_4 = 6 \cdot 10^{-8}$ M. If we denote by G_{H} the yield of radicals of some kind, for example H atoms, expressed as

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

their number per 100 eV of absorbed energy, by C_{AK}, C_{OH}, and C_{H} respectively the average concentrations of the acceptor, OH radicals, and H radicals, and by $\sigma_{\mathrm{AK+H}}$, $\sigma_{\mathrm{H+OH}}$, $\sigma_{\mathrm{H+H}}$ the cross sections of the reactions in which the given radical can participate, then we obtain the equation for the yield of the product of the reaction of the H atom (in the present example) with the dissolved substance:

$$G = G^{\mathrm{H}} \sum \frac{C_{\mathrm{AK}}\sigma_{\mathrm{H+AK}}}{C_{\mathrm{AK}}\sigma_{\mathrm{AK+H}} + C_{\mathrm{OH}}\sigma_{\mathrm{OH+H}} + C_{\mathrm{H}}\sigma_{\mathrm{H+H}}}\,\eta,$$

where G is the yield of the product of the reaction of the acceptor with the H atom, η is the fraction of all radicals reacting at the given average concentration, —in our exam-

at least it is equal to 0.25, and the summation sign includes the sum of four terms corresponding to concentrations $1.5 \cdot 10^{-5}$, $3 \cdot 10^{-6}$, $5 \cdot 10^{-7}$, and $6 \cdot 10^{-8}$ M.

For dilute solutions (less than 10^{-2} M) the radiation-chemical yield of H atoms, G_H, is estimated by the value $G_{\mathrm{H_2O^+}}$, i.e., by the number of ionized water molecules. The initial (left-hand) part of the curves in Fig. 1 is constructed for G_H equal to $G_{\mathrm{H_2O^+}} = 4$ equiv/100 eV. Curve 1 corresponds to the case in which the cross sections for all reactions are taken as maximal and equal to one another, i.e., the chemical interaction between radicals and molecules occurs at each encounter with 100% probability. Such a case

Fig. 1. Dependence of the yield of radiation-chemical transformations on the concentration of acceptor in solution (theoretical calculation).
1 —most active acceptor, **2**, **3** —less active acceptors, **4** —presence of an auxiliary acceptor

Fig. 2. Dependence of the yield of nitrate reduction on the concentration in solution at pH 14 (^{3}) (the theoretical curve is shown by the dashed line)

corresponds to the concept of an "ideal" acceptor. Curve 2 was calculated on the assumption that the cross section for the reaction of a radical (H atom) with an acceptor molecule is 100 times smaller than the cross section for the reaction $\mathrm{H} + \mathrm{AK}$ (poor acceptor). The form of curves 1 and 2 remains strictly identical, but there is a shift into the region of higher concentrations of the dissolved substance. Curve 3 was calculated on the assumption that, along with the main acceptor, an additional acceptor is also present (a competing AK″) at a concentration equal to $10^{-2} M$.

For the calculation it is necessary in this case to introduce into the denominator of the equation given above one more term: $C_{\mathrm{AK''}}\sigma_{\mathrm{AK''+H}}$. The course of this

Fig. 3 and Fig. 4 graphs

Figure 2: Fig. 3 and Fig. 4 graphs

curve practically does not depend on the concentration of free radicals in the track, and the curve has an S-shaped form (in a semilogarithmic coordinate system). Curve 4 corresponds to the assumption, fairly widespread in the foreign literature (^{2}), that H and OH radicals exert the same effect; for example, they are oxidizing agents with respect to ferrous ions.

The rise in the right-hand part of the yield curves in Fig. 1 corresponds to our ideas concerning the participation, together with ionized water molecules, of excited ones. It is assumed that the complete involvement in reactions with the dissolved substance of the dissociation products of 8-9 water molecules is achieved at an acceptor concentration of approximately $4M$. In this case, within one elementary cell of water there is at least one molecule of the dissolved acceptor. At lower concentrations of the dissolved substance, a proportionally smaller fraction of the excited water molecules is involved in interaction with it (provided that there is no transfer of excitation energy from some water molecules to others over distances of several molecular radii).

Figure 2 presents experimental data on the radiation-chemical reduction of nitrate ions in an aqueous solution, published earlier (^3) (solid curve); the calculated curve is shown by dashes; in the initial part they agree satisfactorily. The rise of the experimentally obtained curve in the region of higher concentrations begins earlier, and for sodium nitrate solutions the yield of nitrite reaches a value of 9 keV/100 eV. The early rise in the region of involvement of excited molecules is evidently explained by favorable conditions for transfer of excitation energy from molecules of the medium to molecules entering into the hydration shell.

Fig. 3. Dependence of the yield of reduction of ferric ions on the concentration in solution, pH 3. **1** –in the absence of additives, **2** –in the presence of 1 M glycerol (the theoretical curve is shown by dashes)

Fig. 4. Dependence of the oxidation of ferrous ions in a nitrogen atmosphere on concentration (0.8 NH_2SO_4). **1** –experimental dependence, **2** –oxidizing action of H_2O_2, **3** –oxidizing action of $H_2O_2 + OH$, **4** –oxidizing action of $H_2O_2 + OH + H_2^+$ according to Weiss' s theory

The right-hand part of the curves–the yields of reduction of ferric ions, plotted from the data of A. I. Chernova (Fig. 3)–can be explained by the same considerations.

The left-hand part of these curves corresponds to the case of the presence of a competing acceptor, as indicated by the S-shaped form. Evidently, the competing acceptor in this case is the H^+ ion, which forms with atomic hydrogen molecular ions H_2^+, having a small cross section for reaction with like-charged ferric ions. It should be noted, incidentally, that in the numerous hypotheses (of foreign investigators) advanced to explain the mechanism of reactions involving H_2^+ ions, the electrostatic repulsion between these ions and other positively charged particles (cations) has never been taken into account. Thus, for example, the high yield of oxidation of ferrous ions in the absence of oxygen is explained, according to Weiss' s proposal (^2), by the oxidizing action of the mentioned molecular hydrogen ions. This interpretation is generally accepted and has been used by us as the basis for calculating the curves shown in Fig. 4. Dashed curve **2** corresponds to the fraction of the process of oxidation of ferrous ions by molecular products of the radiolysis of water (hydrogen peroxide), according to the terminology of Allen' s scheme. Curve **3** also takes into account the fraction of oxidation due to interaction with OH radicals. Curve **4** is plotted for the effect of the combined action of H_2O_2, OH radicals, and molecular ions H_2^+. Solid curve **1** is plotted on the basis of experimental data.

data obtained by A. I. Chernova for the concentration dependence of the yield of oxidation of ferrous ions in aqueous solutions saturated with an inert gas. This curve, as is readily seen, coincides with the curve calculated on the basis of the Weiss–Allen hypothesis only over a very narrow concentration range. Its course, as well as the nature of the maximum (about 11 equiv/100 eV), is completely inconsistent with the interpretation given by the Weiss–Allen hypothesis. This is understandable, since the investigators mentioned completely exclude the possibility of the participation of excited molecules, yet allow a number of arbitrary assumptions in order to explain the increased yields by the participation only of ionized water molecules.

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