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Abstract

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THE INFLUENCE OF ACIDITY ON THE YIELD OF RADIATION-CHEMICAL REACTIONS

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Until recently, the dependence of the yield of radiation-chemical reactions on acidity was qualitatively explained on the basis of postulating extremely mobile equilibria of the type

$$H + H^+ \overset{K_a}{\rightleftarrows} H_2^+. \qquad (a)$$

Then the concentrations of the products are determined entirely by the equilibrium conditions and do not depend on the course of the reactions in which they disappear. Consequently, on a plot of $G_{\text{transf}} - f(\text{pH})$ there should be observed some region below which H atoms react in the form of H_2^+, and above it in the form of free H atoms. In the pH region close to pK_a, a sharp change in yield should be observed. Indeed, in a number of works ([1–4]) a similar picture was observed; however, in solutions of different substances different values of pK_a were obtained (from 0 to 3*), which is inexplicable from the indicated point of view. Nor can this point of view explain the observed dependence of the yield on the acceptor concentration, which is usually quantitatively little different from the dependence of G_{transf} on pH.

These difficulties led some investigators, in order to explain the observed regularities, to invoke reactions with negative (“polaron”) and positive ions of water.

The indicated difficulties disappear if it is assumed that the acceptor can compete with the H^+ ion for H atoms:

$$H + Ac \xrightarrow{K_b} \text{products}, \qquad (b)$$

as well as with the dissociation reaction of H_2^+:

$$H_2^+ + Ac \xrightarrow{K_c} \text{products}. \qquad (c)$$

In this case equilibrium (a) will be disturbed as a consequence of the superposition upon it of reactions of radicals and ion-radicals with acceptors. Obviously, such a mechanism can qualitatively explain the different dependence of the yield on the pH of the solution and on the concentration of acceptors in different systems. It is expedient to apply this mechanism to the quantitative description of the kinetics of oxidation and reduction of a mixture of Fe^{2+} and Fe^{3+} ions in a solution saturated with H_2 under pressure, as a function of the pH of the solution. This system has a high sensitivity to changes in pH and in solution concentration and makes it possible to compare with previously obtained data ([6]). For this purpose, the yields of oxidation of Fe^{2+} under the action of γ-rays from Co^{60} on solutions of a mixture of Fe^{2+} and Fe^{3+} ions, saturated with H_2 under pressure, were measured at different acidities of the medium. In addition, an attempt was made in the same way to describe the results obtained by a number of authors ([1–4]) for the dependence of G_{transf} on pH.

* In the work of Allan and Scholes ([5]) on the radiolysis of isopropyl alcohol, a value of $pK_a \simeq 5$ was obtained. We do not consider this work here, since the authors do not provide a substantiated mechanism of radiolysis, without which quantitative treatment of the experimental data is impossible.

The glass cell and the procedure for saturating the solution with hydrogen were described in detail earlier (7). The solutions were prepared from chemically pure reagents in twice-distilled water. Perchlorate solutions were prepared by dissolving spectrally pure iron in $HClO_4$, followed by dilution of the standard solutions to the required concentration. The dose rate of γ-rays from Co^{60} was $\sim 1.75 \cdot 10^{15}$ eV/cm$^3\cdot$ sec. The concentration of Fe^{2+} ions was determined spectrophotometrically with *o*-phenanthroline.

The dependence of the oxidation yield on the concentration of H^+ is given in Table 1.

Table 1

Dependence of $G(Fe^{3+})$ on the concentration of H^+
$[Fe^{3+}] \simeq 10^{-3}M$; $[Fe^{2+}] \simeq 10^{-3}M$; $P_{H_2} = 100$ atm.

Conc. H_2SO_4, mol/l	0.4	0.14	0.029	0.005
$G(Fe^{3+})$, mol/100 eV	6.5	2.9	0	−4
Conc. $HClO_4$, mol/l	0.5	0.2	0.045	10^{-2}
$G(Fe^{3+})$, mol/100 eV	1	−1.25	−4	−4.8

The determinations were carried out in solutions of sulfuric and perchloric acids. The change in the initial concentrations did not exceed 10%. The decrease in the oxidation yield with increasing pH is connected with the competition of the reactions:

$$H + H^+ \xrightarrow{k_1} H_2^+; \tag{I}$$

$$H + Fe^{3+} \xrightarrow{k_2} H^+ + Fe^{2+}. \tag{II}$$

Assuming that the initial yield of Fe^{2+} in the given system is determined by the occurrence of reactions (I), (II), and also

$$H_2^+ + Fe^{2+} \xrightarrow{k_3} H_2 + Fe^{3+}; \tag{III}$$

$$H_2^+ \xrightarrow{k_4} H + H^+; \tag{IV}$$

$$Fe^{2+} + H_2O_2 \xrightarrow{k_5} Fe^{3+} + OH^- + OH; \tag{V}$$

$$Fe^{2+} + OH \xrightarrow{k_6} Fe^{3+} + OH^-; \tag{VI}$$

$$H_2 + OH \xrightarrow{k_7} H_2O + H, \tag{VII}$$

we obtain the equation

$$1 + \frac{k_1[H^+]}{k_2[Fe^{3+}]} \Bigg/ \left(1 + \frac{k_4}{k_3[Fe^{2+}]}\right) =$$

$$= \frac{2\left[G_H + \left(G_{OH} + G_{H_2O_2}\right)/(1 + k_6[Fe^{2+}]/k_7[H_2])\right]}{G_H + G_{OH} + 2G_{H_2O_2} - G(Fe^{3+})} \equiv \frac{2a}{A - G(Fe^{3+})}. \tag{1}$$

The expression on the right-hand side should be a linear function of the value of the ratio $[H^+]/[Fe^{3+}]$. The graphical solution of equation (1) using the data of Table 1 is presented in Fig. 1. For comparison, the graphical solution of equation (1) using the data of (6) on the dependence of $G(Fe^{3+})$ on $[Fe^{3+}]$ in $0.8N$ H_2SO_4 is also given there. The agreement of these data is evident, which makes it possible to assert the correctness of the adopted mechanism.

It is known that in H_2SO_4 solutions the Fe^{3+} ion exists in the form of complexes, which are probably less reactive (8) than free Fe^{3+} ions. Therefore, we determined the dependence of the yield on $[H^+]$ also in hydrochloric acid solutions

Fig. 1

Figure 1: Fig. 1

(Table 1), where Fe^{3+} exists as the free hydrated ion or $FeOH^{2+}_{aq}$. Using the data presented on

Fig. 1, it is possible to determine the actual value $K_1/K_2 = 2.8 \cdot 10^{-3}$.* Let us now try to transfer the idea of a disturbance of the equilibrium $H^+ + H \rightleftharpoons H_2^+$ by reactions of H and H_2^+ with acceptors to other systems in which a sharp dependence of the radiolysis yield on pH is observed. Such a dependence was observed by Hayon and Weiss in the radiolysis of monochloroacetic acid solutions. They also observed a dependence of the yield of the radiolysis products H_2 and HCl on the concentration of monochloroacetic acid. In the authors' opinion, the mechanism of radiolysis includes reaction (I), as well as the reactions

Fig. 1. Graphical solution of equation (1) from the data of Table 1. *a*–H_2SO_4 solutions; *b*–$HClO_4$ solutions; *v*–graphical solution of equation (1) from the data on the dependence of $G(Fe^{3+})$ on $[Fe^{3+}]$ ([6]) in H_2SO_4 solutions

$$H + ClCH_2COOH \xrightarrow{k_8} H_2 + \dot{C}lHCOOH; \qquad \text{(VIII)}$$

$$H + ClCH_2COOH \xrightarrow{k_9} HCl + \dot{C}H_2COOH; \qquad \text{(IX)}$$

$$H^+ + ClCH_2COOH \xrightarrow{k_{10}} H_2 + \dot{C}lHCOOH + H^+. \qquad \text{(X)}$$

Then from the kinetic equations we obtain the expression

$$\frac{k_8}{k_9} + \frac{k_1[H^+]}{k_9[CH_2ClCOOH]} = \frac{G(H_2) - G_{H_2}}{G_H + G_{H_2} - G(H_2)}. \qquad (2)$$

The right-hand side of this expression should be a linear function of the value of the ratio $[H^+]/[CH_2ClCOOH]$. The graphical solution of equation (2) from the experimental data ([1]) is presented in Fig. 2. The tangent of the angle of slope gives $k_1/k_9 \simeq 2.1$; the intercept on the ordinate axis gives the value $k_8/k_9 \simeq 0.25$.

Deighton, Peterson, and Sills observed a dependence of the radiation oxidation of Fe^{2+} and the photochemical oxidation of J^- on pH in solutions of these ions saturated with N_2O. $G\,Fe^{3+}$ is determined by the occurrence of reactions (I), (III)–(IV), and also

Fig. 2. Graphical solution of equation (2) from the experimental data of Hayon and Weiss ([1]). *a*–from data on the effect of pH at a monochloroacetic

Fig. 2

Figure 2: Fig. 2

acid concentration of 0.1 M; b—the same at a concentration of 1 M; v—from data on the effect of the monochloroacetic acid concentration at pH 1

$$N_2O + H \xrightarrow{k_{11}} N_2 + OH; \tag{XI}$$

$$N_2O + H_2^+ \xrightarrow{k_{12}} N_2 + H^+ + OH, \tag{XII}$$

photochemical oxidation of J^- proceeds by reactions (I), (IV), (XI), and (XII), and also

$$J^-_{aq} \xrightarrow{h} J^{-*}_{aq} \xrightarrow{+J^-} J_2^- + OH^- + H; \tag{XIII}$$

$$H_2^+ + J^- \xrightarrow{k_{14}} H_2 + J. \tag{XIV}$$

For both cases the equation is valid

$$1 \Big/ \left[\left(1 + \frac{K_c[Ac]}{k_{12}[N_2O]} \right) + \frac{k_{11}[N_2O]}{k_1[H^+]} \left(1 + \frac{k_4}{K_c[Ac]} \right) \right] = \frac{Q(N_2)}{Q(H_2)} \Big/ \left(1 + \frac{k_{12}[N_2O]}{K_c[Ac]} \right). \tag{3}$$

* Comparison of the data obtained in sulfuric and perchloric acid solutions shows that the effective concentration of the Fe^{3+} ion in sulfuric acid solutions is $\sim 27\%$ of $[Fe^{3+}]_{total}$ and is almost independent of the H_2SO_4 concentration.

In the case of radiolysis of Fe^{2+} solutions,

$K_c[Ac] = k_3[Fe^{2+}]$ and $k_4/k_3 = 1.5 \cdot 10^{-4}$ mole/l. For photolysis of J^-,

$Q(N_2)/Q(H_2) = \varphi(N_2)/\varphi(H_2)$, $K_c[Ac] = k_{14}[J^-]$ and $k_4/k_{14} = 0.1 \pm 0.02$ mole/l ([9]). Reaction (XII), in comparison with reactions (III) and (XIV), was not taken into account.

The graphical solution of equation (3) from experimental data ([2], [3]) is presented in Fig. 3. The slopes of the straight lines give, for K_{11}/K_1, close values: ~ 0.6 and ~ 0.9. From the values of the intercepts cut off on the ordinate axis, we obtain $K_3/K_{12} = 5 \cdot 10^{-2}$ and $K_{14}/K_{12} = 19$.

$$Q(N_2)/Q(H_2) = G(N_2)/[G(H_2) - G_{H2}].$$

For photolysis of Fe^{2+} ion solutions in the presence of acrylic acid (Ak), according to Hayon and Weiss, the process proceeds by the reactions

$$(Fe^{2+}H_2O) \xrightarrow{h\nu} (Fe^{3+}H_2O^-) \xrightarrow{k_{15}} Fe^{3+} + OH^- + H; \qquad \text{(XV)}$$

$$Ak + H \xrightarrow{k_{16}} AkH; \qquad \text{(XVI)}$$

$$AkH + Fe^{3+} \xrightarrow{k_{17}} Ak + Fe^{2+} + H^+, \qquad \text{(XVII)}$$

as well as reactions (I) and (III). Corresponding to this mechanism one can write the equation

$$1 + k_{16}[Ak]/k_1[H^+] = 2\varphi_0(Fe^{3+})/\varphi(Fe^{3+}), \qquad (4)$$

characterizing the dependence of the yield on the pH of the solution. $\varphi_0(Fe^{3+})$ is the quantum yield of Fe^{3+} ions by reaction (XV), and $\varphi(Fe^{3+})$ is the total observed quantum yield. The graphical solution of equation (4) from experimental data ([4]) is presented in Fig. 4. The tangent of the angle of inclination gives $K_{16}/K_1 \simeq 2$.

Fig. 3. Graphical solution of equation (3) from the experimental data of Dainton, Peterson, and Sills: **A** —radiolysis of iron ions ([2]); **B** —photolysis of iodine ions ([3])

Fig. 4. Graphical solution of equation (4) from the data of Hayon and Weiss ([4])

These results show that the radiolysis mechanism, which includes disturbance of the equilibrium

$$H + H^+ \rightleftarrows H_2^+,$$

satisfactorily explains the dependence of the yield on acidity in various systems and, apparently, is of a general character. It does not require invoking reactions with hydrated electrons or positively charged water molecules, which, at least in dilute solutions, probably have time to dissociate before they enter into reactions with the dissolved substance. This conclusion is confirmed by the applicability of the indicated mechanism to photochemical reactions, where the formation of free electrons and positively charged water molecules is excluded.

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