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Abstract

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RADIATION REDUCTION OF FERRIC IONS IN SOLUTIONS SATURATED WITH HYDROGEN UNDER PRESSURE

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In deaerated sulfuric-acid solutions, under the action of radiation, the ion Fe^{3+} undergoes no transformations, since the sum of the oxidizing components $G_{\mathrm{OH}} + 2G_{\mathrm{H_2O_2}}$ is greater than the amount of reducing components, G_{H}; the H_2 formed during radiolysis escapes into the gas phase and does not participate in reactions. Therefore the study of the kinetic characteristics of the Fe^{3+} ion has been carried out in systems containing various additives (1–4). Kinetic treatment of data for such systems is difficult because of their complexity and the large number of competing reactions.

In studies carried out in sulfuric-acid solutions, it was found that the reduction yield depends on the acidity of the solution. The cause of this dependence was not unambiguously established. It is evident that, when molecular hydrogen is present in the solution, some of the OH radicals are transformed into H atoms by the reaction $\mathrm{H_2 + OH \rightarrow H_2O + H}$, thereby increasing the amount of reducing components at the expense of oxidizing ones. In addition, a decrease in the concentration of OH radicals hinders the recombination of radicals with formation of water.

In the present work the yields of reduction of ferric iron in acid solution under the action of γ-radiation from Co^{60} were measured at various concentrations of H_2, Fe^{3+}, and acid.

Method. The investigated Fe^{3+} solution was saturated with hydrogen in a glass cell (5) at atmospheric pressure, after which the cell was sealed and placed in a steel bomb, where the solution was saturated with H_2 at the specified pressure.

Chemically pure reagents were used. The initial solutions were prepared with twice-distilled water. The dose rate was $\sim 3 \cdot 10^{15}$ eV/cm$^3 \cdot$ sec. The concentration of the Fe^{2+} ion was determined by the *o*-phenanthroline method. The extinction coefficient was 10700 l/mol $\cdot$ cm.

Results and discussion. The dependence of the reduction yield on the pressure of H_2 above the solution was determined for a $2 \cdot 10^{-3}$ M solution of Fe^{3+} in

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Fig. 2. Dependence of the reduction yield on the Fe^{3+} concentration

Figure 2: Fig. 2. Dependence of the reduction yield on the Fe^{3+} concentration

0.8 N H_2SO_4. For each H_2 concentration, the initial portions of the reduction curve were recorded. The initial reduction yields calculated from these data are plotted in Fig. 1 as a function of the hydrogen pressure above the solution. As is seen from Fig. 1, the reduction yield increases with increasing pressure. This form of the dependence is explained by competition for OH radicals in the following two reactions:

$$\mathrm{H_2 + OH \xrightarrow{k_1} H_2O + H;} \tag{1}$$

$$\mathrm{H + OH \xrightarrow{k_2} H_2O.} \tag{2}$$

Atomic hydrogen, formed during radiolysis and by reaction (1), participates in the reduction of Fe^{3+} according to the reaction:

$$\mathrm{Fe^{3+} + H \xrightarrow{\mathit{k_3}} Fe^{2+} + H^{+}.} \tag{3}$$

Reaction (3) is competitive with respect to reaction (2). It is obvious that, with an increase in the Fe^{3+} concentration, the reduction yield should increase.

The dependence of the yield on the Fe^{3+} concentration was determined in a 0.8 N solution of H_2SO_4 saturated with H_2 at a pressure of 50 atm. The reduction yields, calculated from the initial portion of the reduction curves, are plotted in Fig. 2 as a function of lg[Fe^{3+}].

Fig. 1. Dependence of the Fe^{3+} reduction yield on the hydrogen pressure above the solution

Fig. 2. Dependence of the reduction yield on the Fe^{3+} concentration

Assuming that the initial yield is determined by the course of the three reactions indicated above, the following expression for the ratio of constants can be derived from the kinetic equations:

$$\frac{k_2}{k_1 \cdot k_3} = \frac{[G_H + G_{\mathrm{OH}} - G(\mathrm{Fe}^{2+})][\mathrm{H}_2][\mathrm{Fe}^{3+}]}{[G(\mathrm{Fe}^{2+}) + G_{\mathrm{OH}} - G_H]\, G(\mathrm{Fe}^{2+}) \cdot M}. \tag{1}$$

In deriving the formula, on the basis of the data of Dale and Sutton (^{6}), it was assumed that the H_2O_2 formed during radiolysis does not have time during irradiation to react to any appreciable extent with the Fe^{2+} ions produced during reduction. But even if all the peroxide reacted during irradiation, equation (1) would change only slightly—instead of the term in the denominator in square brackets, the term $[G(Fe^{2+})+G_{OH}-G_H+2G_{H_2O_2}]$ would appear. However, the Fe^{2+} concentration after irradiation was several units multiplied by $10^{-5}\,M$. At such a concentration, during the irradiation time (3-9 min.) only an insignificant fraction of the peroxide could react.

The irradiated solution was kept for 1 hour after irradiation under pressure. In this process, by the reaction $Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+OH^-+OH$, a certain amount of the Fe^{2+} formed disappears, but the OH radicals produced are transformed by reaction (1) into H atoms, which reduce an equivalent amount of Fe^{3+} ions. Thus, the reduction yield remains unchanged.

From the radiolysis scheme proposed above it follows that the reduction yield should not depend on the acid concentration in the solution. Experimentally, such a dependence was observed in sulfuric-acid solutions. It is known, however, that in sulfuric-acid solutions trivalent iron forms complex ions. It is obvious that the rate constant for the interaction of such an ion with an H atom differs from the rate constant for the free ion. With a change in the H_2SO_4 concentration, the ratio between—

by the amount of free ion Fe^{3+} and complexed ion, which in turn will affect the yield. On the other hand, it is known that in $HClO_4$ solutions the Fe^{3+} ion exists as a free ion. This makes it possible to compare the behavior of the free and the complex ion.

The dependences of the reduction yield on the concentration of H_2SO_4 and $HClO_4$ are shown in Fig. 3. As is seen from Fig. 3, in sulfuric acid solution the yield increases as the concentration of H_2SO_4 decreases, whereas in $HClO_4$ the yield does not change over the entire acid-concentration range studied. The results obtained in $HClO_4$ solutions thus confirm the correctness of the above-proposed radiolysis scheme and of equation (I) derived on its basis.

To establish which of the anions is the complex-forming ion, experiments were carried out with additions of Na_2SO_4 and $NaHSO_4$ to hydrochloric acid solutions. The experiments with added Na_2SO_4 were carried out at high pH so that only a small part of SO_4 was converted into HSO_4^-. In this case only a slight decrease in the reduction yield was observed (Fig. 3), even at concentrations of $SO_4^{2-} \sim 1\,M$. By contrast, the presence of HSO_4^- in an amount of $0.3\,M$* sharply decreases the yield (see Fig. 3). The experiments were carried out in $0.2\,M\,HClO_4$, where the dissociation of HSO_4^- was suppressed. These results make it possible to assert that the complex-forming ion is HSO_4^-. Then, from the data on the dependence of the yield on the concentration of H_2SO_4, one can calculate the equilibrium constant of the reaction:

$$Fe^{3+} + HSO_4^- \overset{K_a}{\rightleftarrows} FeHSO_4^{2+}.$$

Fig. 3. Reduction of Fe^{3+} in solutions with different concentrations of H_2SO_4, $HClO_4$, and in solutions containing additions of Na_2SO_4 and $NaHSO_4$.
1 –H_2SO_4 solution; 2 –$HClO_4$ solution; 3 –$HClO_4 + 0.1\,M\,Na_2SO_4$ solution; 4 –$HClO_4 + 1\,M\,Na_2SO_4$ solution; 5 –$HClO_4 + 0.3\,M\,NaHSO_4$ solution.

From equation (I) the values

$$\frac{k_2}{k_1 \cdot k_3} \cdot \alpha, \quad \text{where} \quad \alpha = \frac{[Fe^{3+}]_{\text{total}}}{[Fe^{3+}]_{\text{free}}}.$$

were calculated. Then, if the quantities α for sulfuric acid solutions with pH 0.4, 0.8, and 1.4 are denoted by α_1, α_2, and α_3, respectively, the ratio $\alpha_1 : \alpha_2 : \alpha_3$ can be determined.

To determine the amounts of trivalent iron existing as free and complex ions, the equation may be written:

$$Fe^{3+}_{\text{free}} + K_a \frac{f_{\text{HSO4}^-} \cdot f_{\text{Fe}^{3+}}}{f_{\text{FeHSO4}^{2+}}} [HSO_4^-][Fe^{3+}]_{\text{free}} = [Fe^{3+}]_{\text{total}}. \tag{II}$$

Using this equation and the ratio $\alpha_1 : \alpha_2 : \alpha_3$, we calculated the value $K_a = 91$ l/mole.

From the experimental data on the dependence of the reduction yield on the concentration of H_2, Fe^{3+}, and H_2SO_4, using equation (I) one can determine the value of the ratio of constants

$$\frac{k_2}{k_1 \cdot k_3} = 71 \pm 5.$$

The concentration of free Fe^{3+} ions for substitution into (I) was calculated from equation (II).

To determine the absolute value of k_3, the following estimate of the absolute values of the constants k_1 and k_2 was made.

Reaction (2) proceeds without activation energy. The steric factor is 0.5. In this case the reaction rate constant, equal to the number

[*] In $0.8\,N$ H_2SO_4 solutions the concentration of the HSO_4^- ion is $\sim 0.3\,M$.

collisions, multiplied by the steric factor, is

$$k_2 = 2.8 \cdot 10^{11} \cdot 0.5 = 1.4 \cdot 10^{11}\ \text{L/mol} \cdot \text{s}.$$

Assuming that the value of k_1 does not change substantially in going from the gas phase to the aqueous phase, we took it from the work of Avraamenko and Lorenzo (^{7}): $k_1 = 2.5 \cdot 10^3$ L/mol · s.

The value calculated on the basis of these data is $k_3 = (8 \pm 0.56) \times 10^5$ L/mol · s.

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