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Abstract

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RADIATION-CHEMICAL REDUCTION OF POTASSIUM FERRICYANIDE IN AQUEOUS SOLUTIONS OF H_2SO_4

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In papers ($^{1-8}$) the mechanism of the radiolytic reduction of potassium ferricyanide in dilute aqueous solutions in the presence of various organic substances (acids, alcohols, amino acids, ketones) was investigated. The role of the organic substance in these studies was mainly reduced to removal of OH radicals from the reaction sphere and to competition with ferricyanide for H atoms and solvated electrons. Czapski and Stein (^{5}), reducing ferricyanide with atomic hydrogen produced in a discharge tube, found that the reduction yield does not depend on pH or on the initial ferricyanide concentration. Independence of the reduction yield from concentration was observed only up to concentrations of $2.6 \cdot 10^{-4}$ *M*. This meant that neither the capture of H atoms by H^+ ions nor the reverse oxidation of ferricyanide, formed upon reduction of ferrocyanide, are capable of competing with the reduction reaction. The value they found for the rate constant of the reduction reaction was of the order of 10^7 l/mole · sec. In the papers of Rabani and co-workers ($^{1,4,6-8}$), the ratio of the rate constants of the reactions was measured:

$$\mathrm{Fe(CN)_6^{3-} + H \rightarrow Fe(CN)_6^{4-} + H^+}, \tag{1}$$

$$\mathrm{RH + H \rightarrow R^{\cdot} + H_2}, \tag{2}$$

where RH is a molecule of the organic substance. The rate constant of reaction (1) in Rabani's experiments was $2 \cdot 10^8$ l/mole · sec. However, a system containing a large number of competing acceptors is rather complex; processes not taken into account in the analysis of the results may occur in it. It seems to us that a system in which OH radicals are completely transformed into hydrogen atoms by the reaction

Fig. 1. Dependence of the amount of ferrocyanide formed on irradiation time during radiolysis of ferricyanide. Initial ferricyanide concentration $16.7 \cdot 10^{-4}$ M, $P_{\mathrm{H}_2} = 10^7$ atm

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Fig. 2

Figure 2: Fig. 2

$$\mathrm{H_2 + OH \rightarrow H + H_2O} \tag{3}$$

(a sufficiently high pressure of hydrogen saturating the solution), and in which the reducing particles formed during water radiolysis are only H atoms (acid medium), proves to be the simplest for studying the mechanism of the radiation-chemical reduction of ferricyanide.

Fig. 1. Dependence of the amount of ferrocyanide formed on irradiation time during radiolysis of ferricyanide. Initial ferricyanide concentration $16.7 \cdot 10^{-4}$ M, $P_{\mathrm{H}_2} = 10^7$ atm.

Experimental procedure. Solutions of $\mathrm{K_3[Fe(CN)_6]}$, additionally purified by repeated recrystallization from twice-distilled water, were prepared in twice-distilled water immediately before the experiment. Radiolytic effects were recorded spectrophotometrically on an SF-4 spectrophotometer at a wavelength of 4200 Å from the decrease in ferricyanide concentration. The extinction coefficient was taken to be 1025 ± 25 at 20°. Irradiation cells were described previously ([10]). Saturation of the solutions with hydrogen under pressure was carried out in a special apparatus by the procedure described—

in the work of V. N. Shubin ([11]). Irradiation was carried out with a Cs^{137} γ-radiation source at a dose rate of $1.93 \cdot 10^{15}$ eV/ml • s, determined with the aid of a Fricke dosimeter ($G(\mathrm{Fe}^{+3}) = 15.6$ ions/100 eV). All experiments were carried out in aqueous solutions of $0.8\,N$ $\mathrm{H_2SO_4}$.

Figure 1 presents the dependence of the amount of ferrocyanide formed under irradiation on the irradiation time. The ferricyanide concentration in this case was $16.7 \cdot 10^{-4}\,M$, and the hydrogen pressure above the solution was 107 atm. The rectilinear portion of the curve in Fig. 1 is retained up to a dose of the order of 10^{18} eV/ml. In this case more than 30% of the ferricyanide is converted, and only then does deviation from the rectilinear dependence begin. The transformation yields of ferricyanide given below were calculated from the rectilinear portions of the accumulation curves.

Fig. 2. Dependence of the reduction yield of ferricyanide on its concentration

at hydrogen pressure. $P_{\mathrm{H2}} = 40$ atm (a, b) and 107 atm (b), dose rate: a—$1.9 \cdot 10^{15}$, b, c—$1.17 \cdot 10^{16}$ eV/ml • s

In order to study the kinetics of the radiolytic transformation of ferricyanide in dilute aqueous solutions, we investigated the influence of the ferricyanide concentration on the yield of its transformation. The results of these investigations are given in Fig. 2. The hydrogen concentration in these experiments was $3.2 \cdot 10^{-2}\,M$ (hydrogen pressure above the solution 40 atm) and $8.6 \cdot 10^{-2}\,M$ (hydrogen pressure above the solution 107 atm).

It is seen from Fig. 2 that the yield of ferricyanide transformation depends on its concentration and, at sufficiently high concentrations, reaches its maximum value, equal to 6 ions/100 eV, i.e., a value close to complete utilization of the H and OH radicals formed during the radiolysis of water is obtained.

Apparently, the results obtained may be interpreted as follows. It is known that ferricyanide can be radiolytically reduced to ferrocyanide, and the latter oxidized to ferricyanide. Since the experiments were carried out in $0.8\,N$ sulfuric acid, in accordance with generally accepted views the products of water radiolysis participating in the subsequent chemical reactions will be hydrogen atoms, hydroxyl radicals, and hydrogen peroxide. The limiting value of the reduction yield, equal to 6 ions/100 eV, which is observed already at a hydrogen pressure of 40 atm, indicates that the concentration of molecular hydrogen attained under these conditions and the ferricyanide concentration corresponding to the maximum reduction yield are quite sufficient to suppress the recombination reaction

$$\mathrm{H} + \mathrm{OH} \rightarrow \mathrm{H_2O}, \tag{4}$$

and hence also the reverse oxidation of ferrocyanide by OH radicals. The same conclusion can be reached from the following considerations. If it is assumed that the observed dependence of reduction on the ferricyanide concentration (Fig. 2) is determined by the participation in the reduction process of reaction (4), then kinetic treatment of the scheme involving reactions (1), (3), and (4) leads to the expression:

$$\frac{k_1(\mathrm{Fe(CN)}_6^{3-})\, k_3(\mathrm{H_2})}{k_4} = \frac{MG(\mathrm{Fe(CN)}_6^{4-})(G_{\mathrm{OH}} + G(\mathrm{Fe(CN)}_6^{4-}) - G_{\mathrm{H}})}{(G_{\mathrm{H}} - G(\mathrm{Fe(CN)}_6^{4-}) + G_{\mathrm{OH}})} = \varphi(G).$$

This expression is the equation of a straight line passing through the origin, in the coordinates $(\mathrm{Fe(CN)}_6^{3-})(\mathrm{H_2})$–$\varphi(G)$. However, upon substituting into this expression the experimentally observed reduction yield, the expected straight line is not obtained (a curve with a steadily increasing ⋯)

angle of inclination). As a result, it may be concluded that reaction (4) does not occur and that a hydrogen pressure of 40 atm is quite sufficient for reaction

(4) not to proceed. In that case the observed decrease in the rate of reduction with dose (Fig. 1) is probably associated with a gradual increase in the concentration of hydrogen peroxide in the solution, which slowly oxidizes the ferricyanide formed. Apparently, under our conditions oxidation of ferrocyanide is also possible by the ion-radical H_2^+. The decrease in the reduction yield when the ferricyanide concentration is lowered can apparently be explained by competition for atomic hydrogen between the reduction reaction and recombination:

$$\mathrm{H} + \mathrm{H} \rightarrow \mathrm{H}_2. \tag{5}$$

To verify that reaction (5) does indeed take place, we investigated the dependence of the reduction yield on the dose rate. According to the $I^{1/2}$ law established by B. V. Ershler (^{9}), if recombination reactions of the type of reaction (5) occur in the irradiated system, and another reaction (of the type of reaction 1) competes with them for the recombining particle, then a dependence of the yield of conversion of the dissolved substance on the radiation intensity should be observed. This dependence should be expressed as a shift of the curve for the dependence of the yield of conversion of the dissolved substance on the logarithm of its concentration, parallel to itself along the logarithmic concentration axis, by an amount equal to $\Delta \lg(I_2/I_1)^{1/2}$. Figure 3 gives the dependences of the ferricyanide reduction yield on the logarithm of its concentration at two different radiation intensities.

Fig. 3. Dependence of the ferricyanide reduction yield on the logarithm of its concentration at constant hydrogen pressure and different radiation intensity. $P_{\mathrm{H2}} = 40$ atm. a—dose rate $1.9 \cdot 10^{15}$ eV/ml • sec, b—$1.17 \cdot 10^{16}$ eV/ml • sec.

As can be seen from the figure, equal values of the reduction yields at the higher radiation intensity are obtained at a higher initial concentration of ferricyanide. According to the $I^{1/2}$ law, the shift along the logarithmic concentration axis (on going to the higher radiation intensity) should be equal to:

$$\lg\left(\frac{11.7}{1.9}\right) = 0.39.$$

Experimentally, a value of 0.35 is obtained, i.e., close to the calculated value. Thus the presence of the $I^{1/2}$ law confirms that reaction (5) does in fact occur.

Thus, the initial reduction yield under our conditions will probably be determined by the course of reactions (1), (3), and (5). Kinetic treatment of this system is very simple and gives the following dependence of the ferricyanide reduction yield on its concentration and on the ratio of the rate constants of reactions (1) and (5):

$$\frac{k_1\,(\mathrm{Fe(CN)}_6^{3-})}{k_5^{1/2}} = \frac{M^{1/2} G\,(\mathrm{Fe(CN)}_6^{4-})}{\left(G_{\mathrm{H}} - G\,(\mathrm{Fe(CN)}_6^{4-}) + G_{\mathrm{OH}}\right)^{1/2}} = \varphi(G). \tag{A}$$

In this expression $(\mathrm{Fe(CN)}_6^{3-})$ is the initial concentration of ferricyanide, M is the conversion coefficient from yield to rate $\left(M = \frac{I}{100N}\right)$, where I is the radiation intensity in eV/l$\cdot$sec, N is Avogadro's number, and G_H, G_OH, $G(\mathrm{Fe(CN)}_6^{4-})$ are, respectively, the yields of atomic hydrogen, OH radicals, and the observed yield of ferricyanide reduction. It is not difficult to note that expression (A) is the equation of a straight line in the coordinates $\varphi(G)$–

$-(\mathrm{Fe(CN)}_6^{3-})$. Fig. 4 is a graphical solution of this equation. From the tangent of the angle of inclination we find that $k_1/k_5^{1/2} = 0.5$. In this case, if we assume that $k_5 = 6\cdot 10^9$ l/mole$\cdot$sec (12), then we shall have $k_1 = 3.9\cdot 10^4$ l/mole$\cdot$sec. The value of the constant k_1 obtained by us differs appreciably from that found by Czapski and Stein (5), and also by Rabani et al. (1,4–8), who used, as acceptors of H atoms competing with ferricyanide, organic substances (formate, ethanol, amino acids, glucose, etc.). The mechanism of the process in such systems is probably much more complex than the authors assumed.

Fig. 4. Graphical solution of equation A

In conclusion, let us compare the values of the rate constants of the reactions of radiolytic reduction of ferricyanide ions and of uncomplexed Fe^{+3} ions. In the work of V. N. Shubin (11) the rate constant was obtained for the reaction:

$$\mathrm{Fe}^{+3} + \mathrm{H} \rightarrow \mathrm{Fe}^{+2} + \mathrm{H}^+. \tag{6}$$

It is equal to $9 \cdot 10^6$ l/mole$\cdot$sec, i.e., approximately two orders of magnitude higher than the rate constant of reaction (1). Such a result seems natural to us, since complex formation can most often lead to stabilization of the valence state of the central ion–the complex former. An analogous effect was observed by us earlier (10) in studying the radiolysis of aqueous ferricyanide solutions.

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