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RADIATION-CHEMICAL OXIDATION OF POTASSIUM FERROCYANIDE IN AQUEOUS SOLUTIONS

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In a number of works the usefulness of applying the method of formal kinetics of Bodenstein–Semenov to elucidate the mechanism of processes occurring in aqueous solutions under the action of radiation has been demonstrated. Application of this method made it possible to clarify in greater detail the mechanism of radiation-chemical transformations of noncomplex ions of divalent and trivalent iron (^{1}-^{3}). The aim of the present study was to apply this method to elucidate the mechanism of radiation-chemical oxidation of the ferrocyanide ion. Fricke and Hart (^{4}), studying the effect of X-radiation on deaerated aqueous solutions of $K_4[Fe(CN)_6]$ in the concentration range 10^{-4}–10^{-1} mole and pH 2 –12, found that the ferrocyanide ion is oxidized to ferricyanide. The oxidation process is accompanied by an increase in pH and the evolution of hydrogen. In a more detailed study of this process (^{5}) under several different conditions, it was established that in the presence of atmospheric oxygen the oxidation yield depends on pH, concentration, and the "age" of the solution. The maximum value of the oxidation yield under these conditions was 7.5 ions per 100 eV. At pH < 11 oxidation of ferrocyanide to ferricyanide was observed, whereas at pH > 11 ferricyanide was reduced to ferrocyanide. Bubbling oxygen through the irradiated solution did not increase the oxidation yield. In the absence of atmospheric oxygen the oxidation yield depended strongly on pH and was considerably smaller than in its presence. In solutions saturated with atmospheric oxygen, a post-effect was observed, the cause of which, as the authors suppose, lies in the accumulation of intermediate oxidation products capable of slowly oxidizing the ferrocyanide ion after irradiation has ceased. In solutions free of atmospheric oxygen, the post-effect was absent. In the works cited, the authors do not give a mechanism for the radiolytic transformations in ferrocyanide solutions.

Fig. 1. Dependence of the amount of formed $K_3[Fe(CN)_6]$ on time at H_2O_2 concentration $= 5.8 \cdot 10^{-4}$ mol/l and $K_4[Fe(CN)_6]$ concentration: 1–$1.60 \cdot 10^{-4}$, 2–$2.66 \cdot 10^{-4}$, 3–$0.26 \cdot 10^{-4}$ mol/l.

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To elucidate the mechanism of the radiation-chemical oxidation of ferrocyanide, it is first of all necessary to determine the kinetics of its reaction with hydrogen peroxide, which, as is known, is one of the products of water radiolysis and in acidic solutions is formed with a yield of 0.8 molecule per 100 eV. In one of the first works (6) devoted to this question, a result was obtained indicating a nonquantitative course of the reaction of oxidation of ferrocyanide by hydrogen peroxide. Per oxidized ferrocyanide ion there was consumed much more than the stoichiometric amount of peroxide. Kistyakovsky (7) found that the rate of the oxidation reaction does not depend on the concentration of ferrocyanide and is a first-order reaction with respect to hydrogen peroxide. The value he obtained for the rate constant

was $5.0 \cdot 10^{-5}$ sec^{-1}. However, Shrikantan and Rao (8) obtained a result contradicting Kistiakowsky’ s conclusions. They found that this reaction is not a first-order reaction, but has a more complex character. Lal (9), assuming that the oxidation proceeds as a first-order reaction, obtained a rate constant equal to $1.35 \cdot 10^{-5}$ sec^{-1}. In his experiments the reaction rate was recorded from the decrease in the peroxide concentration.

Obviously, the discrepancies concerning the order and stoichiometry of this reaction can be explained by the fact that, in the cited works, the concentrations of both ferrocyanide and peroxide were different. It was therefore necessary to eliminate this uncertainty for the conditions under which our radiation-chemical experiments were carried out.

In accordance with this, in nonradiation experiments we used ferrocyanide solutions not exceeding $3 \cdot 10^{-2}$ mol/l and hydrogen peroxide solutions not exceeding 10^{-3} mol.

Procedure. Solutions of $K_4[\mathrm{Fe(CN)}_6]$, additionally purified by recrystallization from twice-distilled water, were prepared with twice-distilled water. Hydrogen peroxide was purified by distillation under vacuum. Peroxide solutions were likewise prepared with twice-distilled water. The solutions under study were prepared immediately before the experiment. The reaction rate was recorded from the increase in the concentration of ferricyanide on an SF-4 spectrophotometer at $\lambda = 420$ mμ (extinction coefficient 1025 ± 25). For radiolytic studies, potassium ferrocyanide was additionally purified and the solutions were prepared with tridistillate.

Fig. 2. Dependence of the amount of $K_3[\mathrm{Fe(CN)}_6]$ formed on irradiation time

Fig. 2. Dependence of the amount of $K_3[\mathrm{Fe(CN)}_6]$ formed on irradiation time at different initial concentrations of ferrocyanide: 1—$5.1 \cdot 10^{-3}$, 2—$7.5 \cdot 10^{-3}$, 3—$1.33 \cdot 10^{-2}$, 4—$2.5 \cdot 10^{-2}$ M.

Figure 2: Fig. 2. Dependence of the amount of $K_3[\mathrm{Fe(CN)}_6]$ formed on irradiation time at different initial concentrations of ferrocyanide: 1—$5.1 \cdot 10^{-3}$, 2—$7.5 \cdot 10^{-3}$, 3—$1.33 \cdot 10^{-2}$, 4—$2.5 \cdot 10^{-2}$ M.

Fig. 3. Dependence of the yield of ferrocyanide on its concentration.

Figure 3: Fig. 3. Dependence of the yield of ferrocyanide on its concentration.

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Hydrogen for saturation was obtained from an electrolyzer and carefully purified of oxygen and organic impurities. The irradiation cell was analogous to that described in ([10]); to one of the outlets of the cell a cuvette for spectrophotometry was sealed on. Irradiation was carried out with a Co^{60} γ-radiation source at a dose rate of $3.66 \cdot 10^{15}$ eV/ml · sec. All results were obtained for solutions containing 0.8 N sulfuric acid.

Fig. 3. Dependence of the yield of ferrocyanide on its concentration.

Figure 1 presents data on the oxidation of the ferrocyanide ion by hydrogen peroxide without irradiation for three different ferrocyanide concentrations. These data show that the rate of the oxidation reaction is constant and, within the limits of experimental error, does not depend on the ferrocyanide concentration, i.e., the reaction proceeds according to first order. In this case one may write:

$$-\frac{dC[\mathrm{Fe(CN)}_6]^{-4}}{dt} = \frac{1}{2} K_0 [\mathrm{H_2O_2}]_\tau,$$

where K_0 is the rate constant, and $[\mathrm{H_2O_2}]_\tau$ is the concentration of hydrogen peroxide at time τ.

The results of calculating the value of the constant K_0 from this equation are presented in Table 1. The obtained value $K_0 = (2.4 \pm 0.4) \cdot 10^{-5}$ sec^{-1} is in good agreement with the data of Lal ([9]). Such coincidence of the rate-constant values may indicate that, under our conditions, the reaction of oxidation of the ferrocyanide ion by hydrogen peroxide proceeds stoichiometrically, since we recorded the reaction rate from the increase in ferricyanide concentration on the assumption that the reaction proceeds stoichiometrically.

Table 1

Effect of the concentration of ferrocyanide ion on the rate constant of potassium ferrocyanide oxidation by hydrogen peroxide

Conc. $K_4[Fe(CN)_6]$, mol/l $\cdot 10^4$	Conc. H_2O_2, mol/l $\cdot 10^4$	$K \cdot 10^5$, $\sec^{-1}$
31.5	6.84	2.54
31.5	6.84	2.49
12.5	6.84	2.34
9.26	5.80	2.00
2.66	5.80	2.76
1.59	5.80	2.76

$$K_{\mathrm{av}} = (2.4 \pm 0.4) \cdot 10^{-5}\ \mathrm{sec}^{-1}.$$

To determine the value of the rate constant of the reaction:

$$[\mathrm{Fe(CN)_6}]^{4-} + \mathrm{OH} \rightarrow [\mathrm{Fe(CN)_6}]^{3-} + \mathrm{OH}^- \tag{1}$$

with OH radicals formed during the radiolysis of water, it is necessary to introduce a competing reaction whose rate constant is known. The following reaction may be chosen as such:

$$\mathrm{H_2} + \mathrm{OH} \rightarrow \mathrm{H} + \mathrm{H_2O}. \tag{2}$$

Then, having obtained the ratio of the constants K_1/K_2, it will be possible to determine K_1.

Figure 2 gives the dependences of the amount of ferricyanide ion formed on the irradiation time. It is evident from the figure that the initial portions of the curves are rectilinear. However, as ferricyanide ion accumulates in the solution, a gradual transition to a stationary state is observed. This is clearly seen in curves 1 and 2, where the initial concentration of ferrocyanide is low. Such a dependence can evidently be expected if, along with oxidation of ferrocyanide, there is a competing reaction in which OH radicals are consumed:

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

Since the experiments were carried out in 0.8 N sulfuric acid, it might have been expected that the H_2^+ ion could participate in the oxidation process. However, it was shown that, for the same initial ferrocyanide concentration, the oxidation yield in neutral solution was higher than in acid. If the H_2^+ ion took part in the oxidation process, the opposite effect should have been observed.

Fig. 4. Graphical solution of equation (A)

To determine the ratio of the rate constants of reactions (1) and (2), experiments were carried out to determine the dependence of the oxidation yield on

Fig. 4. Graphical solution of equation (A)

Figure 4: Fig. 4. Graphical solution of equation (A)

the ferrocyanide concentration at constant hydrogen concentration. From the results of the experiments presented in Fig. 3, it is seen that the oxidation yield increases as the ferrocyanide concentration increases. It was shown above that hydrogen peroxide oxidizes the ferrocyanide ion very slowly. At the initial moment of irradiation, when the peroxide concentration is low, its rapid reaction with atomic hydrogen is more probable:

$$\mathrm{H_2O_2 + H \rightarrow OH + H_2O}. \tag{4}$$

The OH radicals formed in this process will leave the solution via reactions (1) and (3). Since at the initial moment of irradiation the concentration of the ferricyanide formed will be small, it would be natural to assume that, along with reactions (3) and (4), a reaction competing with them also proceeds:

$$\mathrm{H + H \rightarrow H_2}. \tag{5}$$

However, as it turned out, the kinetic expression obtained in this case does not agree with the experimental data. Thus, the initial yield of oxidation under our conditions is determined by the occurrence of the following reactions:

$$\begin{aligned}
&\mathrm{[Fe(CN)_6]^{4-} + OH \rightarrow [Fe(CN)_6]^{3-} + OH}, && (1)\\
&\mathrm{H_2 + OH \rightarrow H + H_2O}, && (2)\\
&\mathrm{H + OH \rightarrow H_2O}, && (3)\\
&\mathrm{H_2O_2 + H \rightarrow H_2O + OH}. && (4)
\end{aligned}$$

From the steady-state conditions for the radicals H, OH and hydrogen peroxide we obtain the following expression:

$$1 + \frac{2K_2[\mathrm{H_2}]}{K_1\{[\mathrm{Fe(CN)_6}]^{4-}\}} = \frac{2G_{\mathrm{H2}}}{G\left([\mathrm{Fe(CN)_6}]^{3-}\right)} = \varphi(G). \tag{A}$$

It is not difficult to see that the expression given is the equation of a straight line that cuts off unity on the axis $2G_{\mathrm{H2}}/G\left([\mathrm{Fe(CN)_6}]^{3-}\right)$. Fig. 4 is the graphical solution of this equation after substitution into it of the experimentally obtained values of the oxidation yield. From the tangent of the angle of inclination we find that $2K_2/K_1 = 18$. Since the value $K_2 = 2.56 \cdot 10^3$ l/mol • sec (1), we find the absolute value of the constant $K_1 = (2.8 \pm 0.2) \cdot 10^2$ l/mol • sec.

Analogous rate constants for the reactions of hydrogen peroxide and OH radicals with noncomplex iron ions are known: $K_{\mathrm{Fe^{+2}+H_2O_2}} = 48 \pm 7$ l/mol • sec (11) and

$K_{Fe^{2+}+OH} = 1.85 \cdot 10^4$ l/mol • sec (²). With this in mind, some conclusions can be drawn concerning the mechanism of oxidation of the ions $[Fe(CN)_6]^{4-}$ by hydrogen peroxide and by OH radicals. The differences in the magnitudes of the rates of the reactions of hydrogen peroxide with the $[Fe(CN)_6]^{4-}$ ion and with the Fe^{+2} ion undoubtedly arise from the very nature of the complex ion and of the attacking particle. As for the radiation-chemical oxidation of the $[Fe(CN)_6]$ ion, which is evidently carried out by OH radicals, complex formation in this case does not have so strong an effect.

The aftereffect observed in the radiolysis of aqueous ferrocyanide solutions in the presence of atmospheric oxygen can be explained by the occurrence of the reactions: $H + O_2 \rightarrow HO_2$, $2HO_2 \rightarrow H_2O_2$, as a result of which peroxide will accumulate, which slowly oxidizes ferrocyanide. This is quite probable, since the ratio of constants K_6/K_3 is approximately 10^5.

As for the mechanism of the charge-transfer act to the OH radical by the $[Fe(CN)_6]^{4-}$ ion in the oxidation reaction, there are still not enough experimental data to resolve this question. However, we are inclined to suppose that in the present case it is not necessary for the attacking particle to enter the inner coordination sphere of the complex ion. It is quite possible that charge can be transferred along the CN bonds. We are led to this by the comparatively large magnitude of the rate constant K_1.

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REFERENCES

1. V. N. Shubin, P. I. Dolin, DAN, **125**, 1298 (1959); **138**, 169 (1961); **139**, 154 (1961); **140**, 1380 (1961).
2. A. O. Allen, W. G. Rothschild, *Radiation Res.*, **7**, 591 (1957).
3. A. O. Allen, V. D. Hogan, W. G. Rothschild, *Radiation Res.*, **7**, 603 (1957).
4. H. Fricke, E. J. Hart, *J. Chem. Phys.*, **3**, 596 (1935).
5. X. Tarrago, E. Marsi, M. Lefort, *C. R.*, **244**, 343 (1957).
6. G. Kassner, *Chem. Ztg.*, **13**, 1701 (1889).
7. W. Z. Kistiakowsky, *Zs. phys. Chem.*, **35**, 431 (1900).
8. B. S. Srikantan, A. R. Rao, *J. Ind. Chem. Soc.*, **10**, 306 (1933).

9. B. B. Lal, *J. Ind. Chem. Soc.*, **16**, 321 (1939).

10. V. N. Shubin, P. I. Dolin, DAN, **134**, 891 (1960).

11. W. G. Barb, J. H. Bakendale et al., *Trans. Farad. Soc.*, **47**, 462 (1951).

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