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The Kinetics of the Autoxidation of Ferrous Ions in Aqueous Tripolyphosphate Solutions

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The kinetics of the autoxidation of ferrous ions in tripolyphosphate solutions (pH 2—8) at an ionic strength of 0.20 M $NaClO_4$ was studied using a spectrophotometric technique. The rate expression for the oxidation reaction is given by:

$$d[Fe(III)]/dt = 4k_I[Fe^{II}(Htpp^{4-})][O_2] + 4k_{II}[Fe^{II}(Htpp^{4-})_2][O_2],$$

and $4k_{II}$ found is to be 1.0×10^2 M^{-1} sec^{-1} at 15°C. The simultaneous reaction paths of

$$Fe^{II}(Htpp^{4-}) + O_2 \xrightarrow{k_I} Fe^{III}(Htpp^{4-}) + O_2^- \text{ and } Fe^{II}(Htpp^{4-})_2 + O_2 \xrightarrow{k_{II}} Fe^{III}(Htpp^{4-})_2 + O_2^-$$

are consistent with the results obtained. When there is an excess of the triphosphate solution in the pH range from 6 to 8, the latter may be the rate-determining step. The acceleration of the oxidation of the ferrous ions in the triphosphate solution may be due to the fact that the stabilization of the oxidation products, $Fe^{III}(Htpp^{4-})$ and $Fe^{III}(Htpp^{4-})_2$, is greater than that of the corresponding ferrous triphosphate complexes. As the activation parameters for the latter reaction, the experiments gave the values of $\Delta H^{\neq} \sim 10$ kcal mol^{-1} and $\Delta S^{\neq} \sim -25$ cal mol^{-1}. deg^{-1}. The negative and relatively small value of the entropy of activation suggests that the activated complex is more extensively hydrated than is the ferrous complex of $Fe^{II}(Htpp^{4-})_2$.

Many workers have reported that the rate of the autoxidation of ferrous ions is dependent upon the species of anions present and on the pH's of the solutions.[1-9] The observed oxidation rates

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[1] J. H. C. Smith and H. A. Spoehr, *J. Am. Chem. Soc.*, **48**, 107 (1926).

[2] H. A. Spoehr, *ibid.*, **46**, 1494 (1924).

[3] J. King and N. Davidson, *ibid.*, **80**, 1542 (1958).

[4] S. Utsumi and K. Muroshima, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 593 (1965).

[5] M. Cher and N. Davidson, *J. Am. Chem. Soc.*, **77**, 793 (1955).

[6] A. M. Posner, *Trans. Faraday Soc.*, **49**, 382 (1953).

[7] A. B. Lamb and L. W. Elder, *J. Am. Chem. Soc.*, **53**, 137 (1931).

[8] R. O. Huffman and N. Davidson, *ibid.*, **78**, 4836 (1956).

[9] P. George, *J. Chem. Soc.*, **1954**, 4349.

of Fe(II), at a given pH, decrease in the order: pyrophosphate,1–4) phosphate,5) chloride,6) sulfate,7,8) and perchlorate.9) The rate, $-\mathrm{d}[\mathrm{Fe(II)}]/\mathrm{d}t$, is first-order with respect to [Fe(II)] and p_{O_2} for the first three anions, while it is second-order with respect to [Fe(II)] and first-order with respect to p_{O_2} for the last two.

King and Davidson demonstrated that the rate for the oxidation of Fe(II) in an acid solution of pyrophosphate at pH's from 1 to 2 is first-order with respect to Fe(II), $\mathrm{H_2P_2O_7}^{2-}$, and dissolved oxygen.3) They also suggested that the effect of the pyrophsophate anions on the oxidation of Fe(II) may be due to the stabilization of such a transition state as $\mathrm{PP\cdots Fe\cdots O_2}$, where PP is the pyrophosphate anion. It was also suggested that the rate, at a given pH, increases with an increase in the affinity of the anion towards ferric ions.3)

In the previous work of this series, our finds on the oxidation of Fe(II) by dissolved oxygen in aqueous solutions in the presence of a chelating-agent were reported; these findings showed a linear relationship between the logarithmic rate constant and the $\log R_f$ value.10),*1 Further extension of the work on the autoxidation of Fe(II) accelerated by the triphosphate anion was attempted spectrophotometrically; in this paper the mechanism of the reaction will be postulated.

Experimental

Materials. The ferrous ammonium sulfate, perchloric acid, sodium perchlorate, ferric ammonium sulfate, and sodium hydroxide were available G. R.-grade reagents. The sodium triphosphate was recrystallized five times from a 25% aqueous solution of ethanol. The purity of the sodium triphosphate ($\mathrm{Na_5P_3O_{10}\cdot 6H_2O}$), as determined by means of anion exchange chromatography,11) was above 98%. Redistilled water was used in preparing all the solutions.

Determination of Total Fe(III). The effect of the pH upon the absorption spectra of ferric ion species at wavelengths from 230 mμ to 350 mμ in an excess of triphosphate (TPP) is shown in Fig. 1. The isosbestic point at 260 mμ is invariable throughout the pH region between 2 and 7. Within this pH region, the total concentration of the ferric ions produced by the oxidation of ferrous ions can be determined by the absorption intensity at 260 mμ, whose molar extinction coefficient is 4620 $\mathrm{M^{-1}cm^{-1}}$. In order to estimate the concentration of ferric ions at a pH value higher than 7, the value of a molar extinction coefficient at 260 mμ depending on the pH was found and used. For the purpose of determining the composition of the TPP complex of ferric ions, the molar-ratio method was applied; the results are shown in Fig. 2. The evidence shown in Fig. 2, in which the optical density becomes nearly constant at [TPP]/[Fe(III)] values higher than 2, suggests that the composition of the Fe(III) complex with the highest number of complexing agents is $\mathrm{Fe^{III}}$-$\mathrm{(TPP)_2}$.

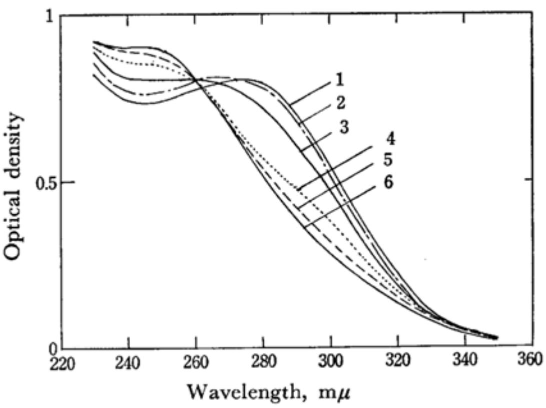

Fig. 1. Absorption spectra of the Fe(III)-TPP complex in exess of the TPP solutions.
1.33×10^{-4} M Fe(III), 1.66×10^{-2} M TPP, 0.20 M $\mathrm{NaClO_4}$, 15°C
pH : 1 7.93 2 5.68 3 4.35
4 2.95 5 2.35 6 1.92

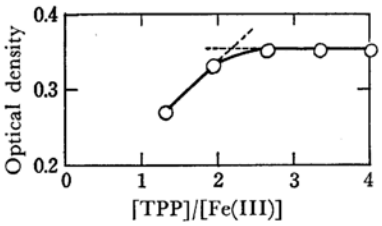

Fig. 2. Variation of the optical densities with [TPP]/[Fe(III)].
7.60×10^{-5} M Fe(III), 0.20 M $\mathrm{NaClO_4}$,
pH$=5.62\pm0.02$, room temperature

Rate Determination. Except for a few cases, the ionic strength of the TPP solutions was kept at 0.207 by sodium perchlorate. About 50 m*l* of the TPP solution was taken into a 100-m*l* beaker and the pH of this solution was adjusted by the addition of a few drops of dilute perchloric acid or dilute sodium hydroxide. Appropriate amounts of a freshly-prepared aqueous solution of ammonium ferrous sulfate and 25 m*l* of the TPP solution were kept in a thermostated bath at 15°C for about one hour in order to saturate these solutions with air. Then, reaction was initiated by the addition of 1 m*l* of the Fe(II) solution into the stirred TPP solution by means of an injection syringe. The ionic strength of the reaction mixture was 0.20. The progress of the oxidation reaction was followed spectrophotometrically at 260 mμ using a Hitachi recording spectrophotometer. The recording of the absorption intensity of the Fe(III) produced could be started within nine seconds after the initiation of the reaction. The pH value of the reaction mixture was measured using a Hitachi-Horiba F-5-type pH meter. The reaction rate

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*1 R_f represents the ratio of the chelate formation constant for the Fe(III) to that for the Fe(II) ($K_{\mathrm{Fe^{III}L}}/K_{\mathrm{Fe^{II}L}}$).

10) Y. Kurimura, R. Ochiai and N. Matsuura, This Bulletin, **41**, 2234 (1968).

11) N. Matsuura, Y. Kurimura and K. Kiyokawa, *Bunseki Kagaku (Japan Analyst)*, **16**, 612 (1967).

in an oxygen-saturated solution was observed according to a procedure described previously.[10]

Results and Discussion

Variations in the optical densities of the Fe(III)-triphosphate complex at 260 mμ in aerated solutions initially containing TPP and various initial concentrations of Fe(II) are shown in Fig. 3. The initial oxidation rate, d[Fe(III)]/dt, was determined from the slope of the starting curve. A linear relationship between the oxidation rate and the Fe(II) concentration holds well except when the total concentration of the Fe(II) is relatively higher than that of the TPP. This linear relationship indicates a pseudo-first-order dependence of the rate on the Fe(II) concentration at any particular pH value.

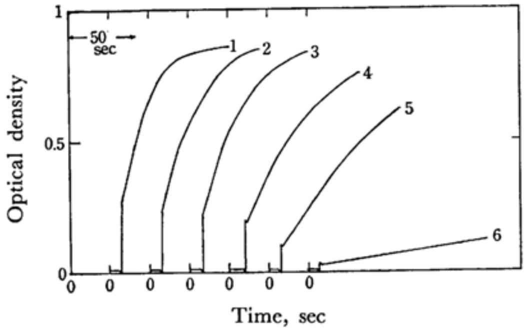

Fig. 3. Variation of the optical densities with the reaction times.
2.0×10^{-2} M TPP, 2.0×10^{-4} M Fe(II), 0.20 M $NaClO_4$, 15°C
pH : 1 8.77 2 8.29 3 6.36
4 5.31 5 4.61 6 3.41

A comparison of the oxidation rates in aerated and oxygenated solutions is tabulated in Table 1. A first-order dependence of the rate on the oxygen concentration is observed since the ratio of the obtained rates on these two solutions, R_O/R_A, is about 4.9; this value agrees with the theoretical value of the ratio of the oxygen concentration in the oxygenated and in the aerated solutions, which is evaluated as 4.76 : 1. The results obtained by varying the pH value are shown in Fig. 4. With an increase in the pH value, the rate increases markedly in the pH region between 2 and 6, finally attaining a limiting value at a pH higher than 6. Simillar rate dependences on the pH were observed in the oxygen oxidation of such Fe(II)-chelates as Fe(II)NTA and Fe(II)-EDTAOH.[10]

TABLE 1. COMPARISON OF THE OXIDATION RATES IN THE AERATED (R_A) AND THE OXYGENATED (R_O) SOLUTIONS (10^{-6} M sec^{-1})
2.0×10^{-4} M Fe(II), 2.0×10^{-2} M TPP, pH$=4.01\pm0.02$, room temperature

R_A	R_O	R_O/R_A
0.63	3.10	4.93
0.64	3.05	4.86
	mean	4.89

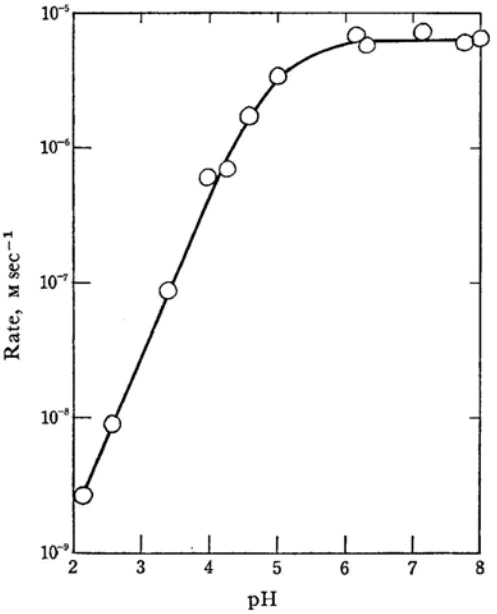

Fig. 4. Dependence of the oxidation rate on the pH.
2.0×10^{-2} M TPP, 2.0×10^{-4} M Fe(II), 0.20 M $NaClO_4$, 15°C

In these Fe(II)-chelates systems, such an increase in the rate may be attributed to an increase in the concentration of the chelated Fe(II) with the pH value. Generally, Fe(II)-chelates are oxidized more rapidly by oxygen molecules in acid and neutral aqueous solutions than are aquo ferrous ions.[10]

In order to obtain information on the order of the oxidation reaction, Job's continuous variation method[12] was employed. The results with this method are shown in Fig. 5. In this figure, the oxidation rates are plotted against the ratio of the concentrations, [Fe(II)]/{[Fe(II)]+[TPP]}, which is represented by R, the dominator of which is kept at a constant value of 5.0×10^{-4} M. A maximum is observed at R ~0.3 on the curve; this indicates that the reaction is first-order with respect to the free Fe(II) concentration and second-order with respect to the free TPP concentration at a given pH and at a given concentration of the dissolved oxygen. The small shoulder observed around R ~0.5—0.7 suggests the other rate dependence, which is first-order with respect to the concentrations of the free Fe(II) and the free

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[12] P. Job, *Ann. Chim.*, **6**, 97 (1936).

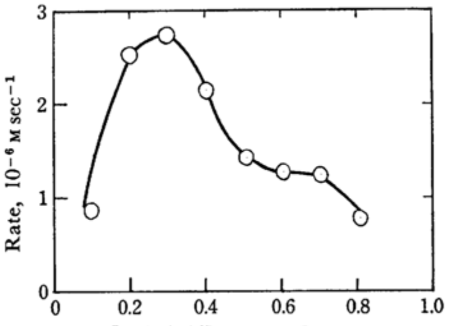

Fig. 5. Kinetic method of continuous variations. $[Fe(II)]+[TPP] = 5.0\times10^{-4}$ M, 0.20 M $NaClO_4$, $pH=6.80\pm0.03$, 15°C

TPP respectively.

From the results obtained, the rate equation at a given pH can be written as:

$$\frac{d[Fe(III)]}{dt} = k_a[Fe(II)]_f[TPP]_f[O_2] + k_b[Fe(II)]_f[TPP]_f^{\,2}[O_2] \qquad (1)$$

where $[Fe(II)]_f$ and $[TPP]_f$ are the concentrations of the free ferrous ion and the free triphosphate ion respectively, and where k_a and k_b are apparent rate constants.

Under the present experimental conditions, five species of the triphosphate, H_5tpp, H_4tpp^-, H_3tpp^{2-}, H_2tpp^{3-}, and $Htpp^{4-}$, must be considered in the solution, while the completely dissociated species of tpp^{5-} can be disregarded. Fractions of the triphosphate species are calculated using the stability constants of triphosphoric acid;*2 these are plotted in Fig. 6 as a function of the pH value.

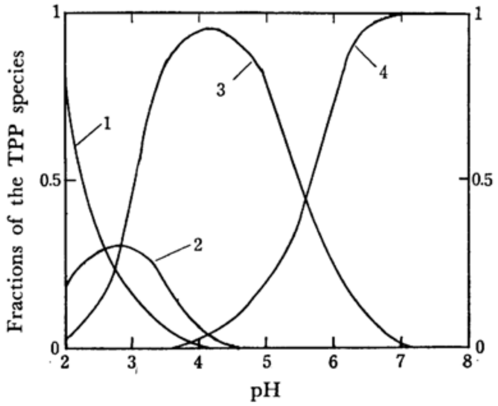

Fig. 6. Fractions of the TPP species *vs.* pH curve.
1: H_4tpp^- 2: H_3tpp^{2-} 3: H_2tpp^{3-} 4: $Htpp^{4-}$

From a comparison of the rate-pH curve (Fig. 4) and the fraction-pH curve (Fig. 6), it is clear that the increase on the oxidation rate corresponds to the increase in the fraction of the H_4tpp^{4-}. This evidence suggests that the free TPP species in the rate equation (1) is $Htpp^{4-}$. It is reasonable to conclude from the results obtained that complex species of $Fe^{II}(Htpp^{4-})_2$ and $Fe^{II}(Htpp^{4-})$ are formed in the Fe(II)-TPP solution and that these are oxidized predominantly by dissolved oxygen. The quadratic dependence of the rate on the $Htpp^{4-}$ concentration, seen in the rate equation (1), is quite difficult to explain from kinetic point of view if complex formation between the Fe(II) and the TPP is not considered.

The reaction scheme most suited to the experimental results indicates two pre-equilibrium reactions, (2) and (3), and the simultaneous reaction paths of (4) and (5) (the (4) and (5) reactions are the rate-determining steps of the oxidation reaction):

$$Fe^{2+} + Htpp^{4-} \rightleftarrows Fe^{II}(Htpp^{4-}) \qquad (2)$$

$$Fe^{II}(Htpp^{4-}) + Htpp^{4-} \rightleftarrows Fe^{II}(Htpp^{4-})_2 \qquad (3)$$

$$Fe^{II}(Htpp^{4-}) + O_2 \xrightarrow{k_I} Fe^{III}(Htpp^{4-}) + O_2^- \qquad (4)$$

$$Fe^{II}(Htpp^{4-})_2 + O_2 \xrightarrow{k_{II}} Fe^{III}(Htpp^{4-})_2 + O_2^- \qquad (5)$$

$$O_2^- + H^+ \rightleftarrows HO_2 \qquad (6)$$

$$Fe(II) + HO_2(\text{or } O_2^-) \rightarrow \text{further oxidation (fast)} \qquad (7)$$

The oxidation of the Fe(II) by the HO_2 or O_2^- radical may proceed by means of Weiss's mechanism.[14,15] If so one molecule of O_2 oxidizes four atoms of the Fe(II). The above mechanism is also consistent with the results shown in Table 2, which shows little dependence of the rate on the ionic strength of the solution. Although the formation constant of the triphosphate complex of the ferrous ion has not yet been reported, complex formation between Fe(II) and TPP can be expected from the evidence that several divalent metal ion (Ba^{2+}, Cd^{2+}, Ca^{2+}, and Co^{2+}) complexes of the triphosphate with relatively greater stabilities

TABLE 2. RELATIONSHIP BETWEEN THE OXIDATION RATE AND THE IONIC STRENGTH
2.0×10^{-2} M TPP, 2.0×10^{-4} M Fe(II), $pH=5.90\pm0.02$, 15°C

Ionic strength	Oxidation rate, 10^{-6} M sec^{-1}
0.20	7.8
0.25	8.0
0.50	8.4
1.00	10.0

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*2 $\log K^H_{H_4L}=0$, $\log K^H_{H_3L}=2.6$, $\log K^H_{H_2L}=2.7$ and $\log K^H_{HL}=5.6$ and $\log K^H_L=7.9$ $(\mu=0.1)$.[13]

13) A. E. Martell and G. Schwarzenbach, *Helv. Chim. Acta*, **39**, 653 (1956).

14) J. Weiss, *J. Chim. Phys.*, **48**, C-6 (1951).

15) J. Weiss, *Experientia*, **IX**, 61 (1953).

have been reported.[16-18] The proposed rate expression for the oxidation reaction is:

$$\frac{\mathrm{d[Fe(III)]}}{\mathrm{d}t} = 4k_{\mathrm{I}}[\mathrm{Fe^{II}(Htpp^{4-})}][\mathrm{O_2}] + 4k_{\mathrm{II}}[\mathrm{Fe^{II}(Htpp^{4-})_2}][\mathrm{O_2}] \qquad (8)$$

The first term in this quation may be neglected in an excess of the TPP solution in the pH region between 6 and 8 since the concentration of the $\mathrm{Fe^{II}(Htpp^{4-})_2}$ is nearly equal to the total concentration of the Fe(II) (Fig. 5). The k_{II} value is then evaluated by dividing the oxidation rate, which is obtained in an excess of the TPP solution at pH 6—8, by the total concentration of the Fe(II) and by the oxygen concentration.[*3] The k_{II} value thus obtained is 25 $\mathrm{M^{-1}\,sec^{-1}}$ at 15°C.

As has previously been reported,[10] the accelaration of the oxidation of ferrous ions in the presence of such chelating agents as EDTA, EDTAOH, and DTPA may be attributed to the lowering of the free energy of the activation ($\Delta G^{\neq}$) of the rate-determining step of the reaction of the following type due to the fact that the ferric state is more stable than the corresponding ferrous state:

$$\mathrm{Fe^{II}Z + O_2 \rightarrow Fe^{III}Z + O_2^-} \qquad (9)$$

where $\mathrm{Fe^{II}Z}$ and $\mathrm{Fe^{III}Z}$ are ferrous and ferric chelates respectively. The effect of the triphosphate anion on the oxidation of ferrous ions also seems to be attributable to a lowering of the $\Delta G^{\neq}$ values of the reaction (4) and reaction (5) by complex formations. As the activation parameters for the reaction (5), $\Delta H^{\neq} \sim 10$ kcal mol^{-1} and $\Delta S^{\neq} \sim -24$ cal mol^{-1} deg^{-1} are obtained from the temperature dependence of the rate constant, as may be seen in Table 3. The relatively small negative value of the activation entropy suggests that the activated complex formed at the transition state in (5) is more extensively hydrated than the ferrous complex, probably as a result of the cleavage of the Fe–O bond in the ferrous complex. Analogous to the oxidation reaction discussed here, it is reasonable to suggest that the acceleration of the oxidation of the Fe(II) by the pyrophsophate anion in a relatively high pH region is due to complexation between the Fe(II) and the pyrophosphate anion.

TABLE 3. TEMPERATURE DEPENDENCE OF THE OXIDATION RATE

2.0×10^{-2} M TPP, 2.0×10^{-4} M Fe(II), pH$=4.51\pm0.01$, 0.20 M $\mathrm{NaClO_4}$

$(1/T)\times10^3$	Rate constant (k_{II}, $\mathrm{M^{-1}\,sec^{-1}}$)
3.47	25
3.37	41
3.31	53

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16) J. A. Wolhoff and J. T. G. Overbeek, *Rec. Trav. Chim.*, **78**, 759 (1959).

17) J. I. Watters and S. M. Lambert, *J. Am. Chem. Soc.*, **81**, 3201 (1959).

18) A. Jansson and E. Wännien, *Tranta,* **10**, 769 (1963).

[*3] The concentration of oxygen in the air-saturated solution is estimated to be 2.9×10^{-4} M at 15°C.