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Oxygen Oxidation of Ferrous Ions Induced by Chelation

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The oxidation of ferrous ions by dissolved oxygen in aqueous solutions in the presence of such chelating agents as EDTA, DTPA, EDTAOH, EDTP, CyDTA and NTA was studied spectrophotometrically. The rate equation for the oxidation reaction is:

$$d[\mathrm{Fe^{III}}]/dt = 4k_p[\mathrm{Fe^{II}HZ}][\mathrm{O_2}] + 4k_n[\mathrm{Fe^{II}Z}][\mathrm{O_2}]$$

where k_p is the rate constant for the (1) reaction; k_n, the rate constant for the (2) reaction; $\mathrm{Fe^{II}HZ}$, protonated chelate, and $\mathrm{Fe^{II}Z}$, the normal chelate.

$$\mathrm{Fe^{II}HZ} + \mathrm{O_2} \xrightarrow{k_p} \mathrm{Fe^{III}Z} + \mathrm{HO_2} \tag{1}$$

$$\mathrm{Fe^{II}Z} + \mathrm{O_2} \xrightarrow{k_n} \mathrm{Fe^{III}Z} + \mathrm{O_2}^- \tag{2}$$

The linear relationship between $\log k$ and $\log R_f$ shown by Eq. (3), was obtained from all the experimental results except for those on the EDTPA and CyDTA systems:

$$\log k = 0.92 + 0.13 \log R_f \tag{3}$$

In Eq. (3), k is $4k_p$ and R_f is $K_{\mathrm{Fe^{III}L}}/K_{\mathrm{Fe^{II}HL}}$ for the protonated chelate, while k is $4k_n$ and R_f is $K_{\mathrm{Fe^{III}L}}/K_{\mathrm{Fe^{II}L}}$ for the normal chelate. In the cases of the DTPA and CyDTA systems, a deviation from the straight line was observed. This can be explained by steric hindrance of the oxygen attack by these chelates.

The oxidation of ferrous ions by dissolved oxygen in aqueous solutions in the presence of simple anions, such as chloride,(1) sulfate,(2) perchlorate(3) and phosphate,(4) has been extensively investigated. The oxidation reaction has been found to be accelerated in the presence of pyrophosphate anions.(5-8) King and Davidson suggested that the oxidation rate of ferrous ions increases as the complexing affinity of the anion for ferric ions increases.(7) Thus, at a given pH, the rate can be found to decrease in the order of pyrophosphate, phosphate, chloride, sulfate, and perchlorate.

The oxidation reaction is also accelerated in the presence of such chelating agents as ethylenediaminetetraacetic acid (EDTA), nitritotriacetic acid (NTA), diethylenetriaminepentaacetic acid (DTPA), 1,2-cyclohexanediaminetetraacetic acid (CyDTA), *N*-Hydroxyethylenediamine-*N*,*N*′,*N*′-triacetic acid (EDTAOH), and ethylenediaminetetrapropionic acid (EDTP). This acceleration may be ascribed to the stabilization of the oxidized form by the chelation. In this connection, a relationship between the oxidation rate of ferrous ions and the chelation of ferrous and ferric ions is expected. The rate and mechanism of the oxidation reaction of ferrous ions by dissolved oxygen were studied spectrophotometrically; the effect on the reaction rate of the chelation of ferrous and ferric ions will also be discussed.

Experimental

Materials. The ferrous ammonium sulfate, perchloric acid, and sodium hydroxide used were all commercially-available G. R.-grade reagents. Redistilled water was used in the preparation of the solutions.

Preparation of Samples. The hydrogen ion concentration in the chelating-agent solution containing sodium perchlorate was adjusted by the addition of dilute perchloric acid or a dilute sodium hydroxide

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1) A. M. Posner, *Trans. Faraday Soc.*, **49**, 382 (1953).

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

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

5) H. A. Spoehr, *ibid.*, **46**, 1497 (1924).

6) J. H. C. Smith and H. A. Spoehr, *ibid.*, **48**, 107 (1926).

7) J. King and N. Davidson, *ibid.*, **80**, 1542 (1958).

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

solution. A ferrous ion solution was prepared by mixing appropriate amounts of a ferrous ammonium sulfate solution, a sodium perchlorate solution, and water. The ionic strengths of these solutions were maintained at 0.1 by sodium perchlorate.

Measurement of Reaction Rate. The chelating agent and the ferrous ion solutions were kept in a thermostated bath at 25°C for about one hour. By the mixing of the air-saturated chelating-agent and the air-saturated ferrous ion solutions, the reaction was initiated. A portion of the reaction mixture was poured into a 1-cm quartz cell, and the variation in the optical density in the ultraviolet region due to the ferric chelate was recorded automatically on a Hitachi recording spectrophotometer. Thus, twelve seconds after the initiation of the reaction, reproducible results could be obtained. When the reaction proceeded at a moderate rate, the variation in the optical density was measured by using a Hitachi EPU-type spectrophotometer. The molar extinction coefficients used to determine the concentrations of the ferric chelates of EDTA, NTA, DTPA, CyDTA, EDTAOH, and EDTP were 9300 at 258 mμ, 7100 at 258 mμ, 9600 at 258 mμ 8200 at 260 mμ 7900 at 259 mμ, and 5600 at 258 mμ respectively. The variation in the molar extinction coefficients of these chelates under the present experimental conditions was within ±3% in each case.

The oxidation rates in the oxygen-saturated solutions were determined by the following procedure. A 20 m*l* test tube with two small pipes at the end of its was used. These pipes were used to bubble oxygen gas through the solution. One of the test tubes was used for the oxygenation of the ferrous-ion solution, and the other, for the oxygenation of the chelating agent solution. Oxygen bubbling was continued about two hours at 25°C. Then, one or two m*l* of the ferrous ion solution were pipetted into 10 m*l* of the chelating agent solution, in which oxygen bubbling was continued until the end of the measurements. A portion of the oxygen-saturated reaction mixture was poured into a 1 cm quartz cell equipped with a cap. The variation in the optical density was measured in the manner described above.

Results

Dependence of the Rate on the Concentrations of Ferrous Ions, Chelating Agent, and Oxygen. The variation in the ferric-ions concentration with the time at various concentrations of ferrous ions at a given pH and a given concentration of the chelating agent for the DTPA system is shown in Fig. 1. The initial oxidation rate was determined from the initial slope of the curve. The dependence of the rate on the concentration of Fe(II) for the DTPA system is shown in Fig. 2. A linear relationship between the rate and the concentration of Fe(II) was observed in this case. A linear relationship was also obtained between the rate and the concentration of the chelating agents, as Fig. 3 shows.

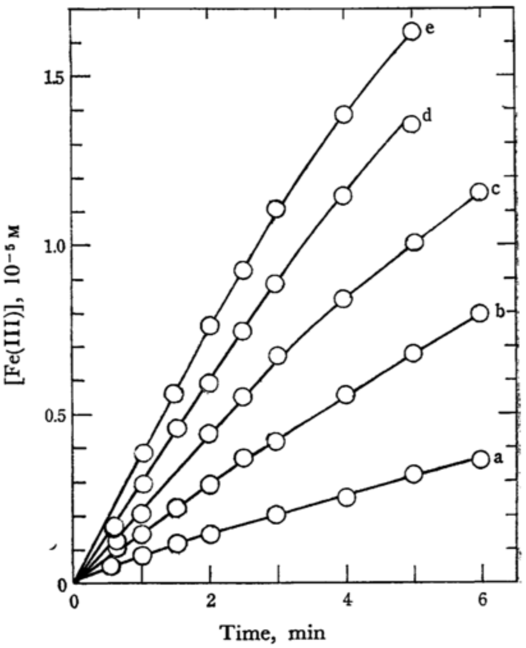

Fig. 1. Variation of the Fe(III) concentrations with time in the air saturated Fe(II)-DTPA system.
Fe(II) concentration:
a 8.0×10^{-6} M b 1.2×10^{-5} M c 1.6×10^{-5} M
d 2.4×10^{-5} M e 4.0×10^{-5} M
1.06×10^{-4} M DTPA pH 2.30±0.01
0.1 M $NaClO_4$ 25°C

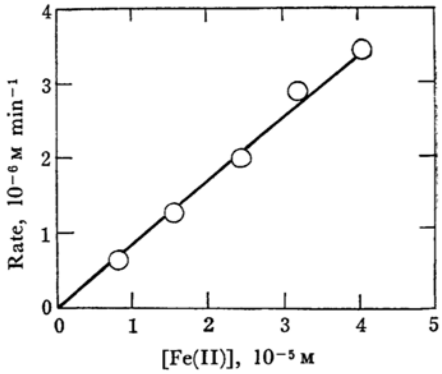

Fig. 2. Dependence of the oxidation rate on Fe(II) concentration in the air saturated Fe(II)-DTPA system at low pH region.
1.06×10^{-4} M DTPA pH 2.30±0.01
0.1 M $NaClO_4$ 25°C

Under the present experimental conditions, the reaction was first-order with respect to the total concentrations of both ferrous ions and the chelating agent. However, this linear relationship was not observed in the relatively high pH region.

The oxidation reaction in these systems was also first-order with respect to the concentration of dissolved oxygen in the solution. This first order dependence was examined by comparing the specific rate in the air-saturated solution with that in the oxygen-saturated solution. The ratio of the concentrations of oxygen in the aerated and

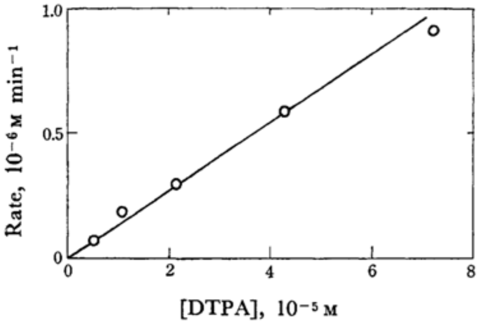

Fig. 3. Dependence of the oxidation rate on DTPA concentration in the air saturated Fe(III)-DTPA system at low pH region.
4.0×10^{-5} M Fe(II) pH 2.22 ± 0.01
0.1 M $NaClO_4$ 25°C

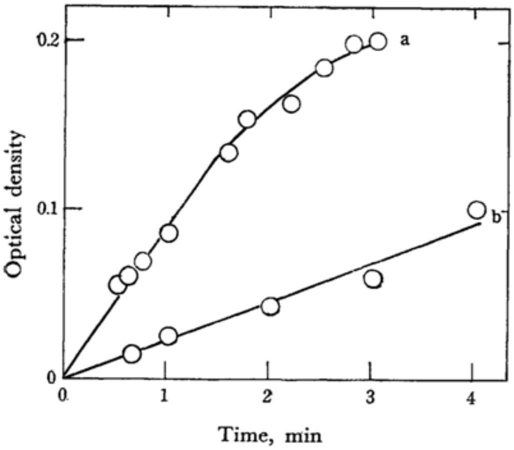

Fig. 4. Comparison of the oxidation rate in the air saturated solution and in the oxygen saturated solution.
a oxygen saturated solution
b air saturated solution
pH 2.00 ± 0.01 0.1 M $NaClO_4$ 25°C

oxygenated solutions was estimated to be about 1 to 4.7. This ratio was nearly equal to the ratio of the reaction rate in an aerated solution to that in the corresponding oxygenated solution, as is shown in Fig. 4 for the DTPA system.

The results suggested that the rate equation for Fe(II)-chelating agent-O_2 reaction system at a low pH is:

$$d[\mathrm{Fe(III)}]/dt = k_a[\mathrm{Fe(II)}]_t[\mathrm{Z}]_t[\mathrm{O_2}] \quad (1)$$

where k_a is the apparent rate constant; $[\mathrm{Fe(II)}]_t$, the total concentration of the ferrous iron, and $[\mathrm{z}]_t$, the total concentration of the chelating agent.

Dependence of the Rate on the pH. The variation in the rate with the pH in the DTPA, EDTA, CyDTA, and EDTAOH systems is shown in Figs. 5 and 6. The reaction rate in the EDTA system in the pH region from 3 to 5 under these experimental conditions could not be deterimned because the rate was too rapid to determine its value. The oxidation rate in the DTPA system, as shown in Fig. 5, increases simply with an increase pH values of the solution under the conditions employed and reaches its maximum at pH 4. Then, with the increase in the pH, the rate begins to decrease, becoming nearly constant at pH values higher than 6.5. In the EDTA and the CyDTA systems, such a maximum in the reaction rate was also observed. On the other hand, under these experimental conditions the reaction rates in the NTA and the EDTAOH systems increase simply with an increase in the pH values and become nearly constant at higher pH values, without any distinctive maximum.

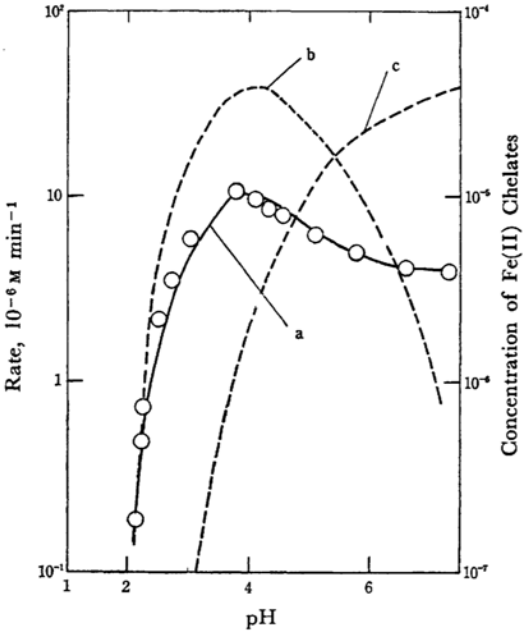

Fig. 5. Dependence of the oxidation rate on pH in the air saturated Fe(II)-DTPA system.
○ observed value
a calculated curve
b concentration of protonated chelate ($Fe^{II}HDTPA$)
c concentration of normal chelate ($Fe^{II}DTPA$)
9.4×10^{-4} M DTPA 4.0×10^{-5} M Fe(II)
0.1 M $NaClO_4$ 25°C

Discussion

The concentrations of Fe(II) chelate for the EDTA and the DTPA systems under the present experimental conditions can be calculated by using the formation constants of Fe(II) chelates and the acid dissociation constants of the chelating agents. The results of the calculation are shown in Fig. 5 for DTPA chelates. By comparing these two curves with the observed rate, it is made clear that the oxidation reaction of Fe(II) chelates proceeds

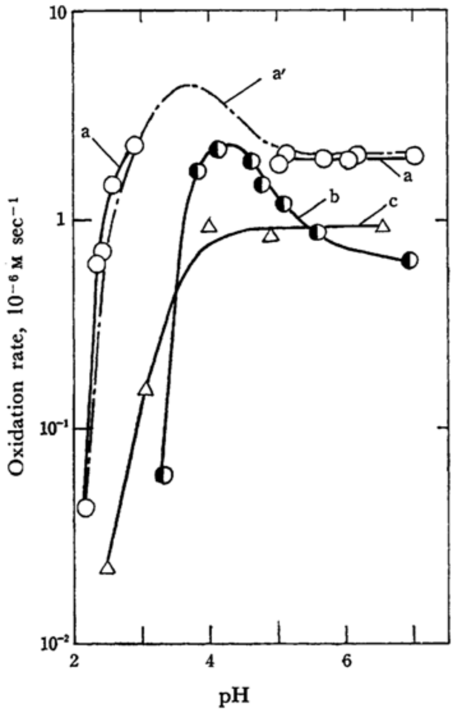

Fig. 6. Dependence of the oxidation rate on pH in the air saturated Fe(II)-chelating agent systems.
a EDTA system, 3.1×10^{-5} M EDTA
a' calculated curve for the EDTA system
b CyDTA system, 4.6×10^{-5} M CyDTA
c EDTAOH system, 1.5×10^{-4} M EDTAOH
2.9×10^{-5} M Fe(II) 0.1 M $NaClO_4$ 25°C

through two simultaneous reaction paths, one of which involves the oxidation of the protonated chelate while the other involves the oxidation of the normal chelate. In a similar way, it may be suggested that the oxidation of Fe(II) in the EDTA system also preceeds through two simultaneous reaction paths. The maximum in the oxidation rate for the CyDTA system, shown in Fig. 6, indicates the presence of the protonated chelate in a low pH region, though the formation constant of the protonated chelate has not yet been reported. As is clear from the foregoing discussion, the rate equation (2) can be assumed for the oxidation of Fe(II) chelates discussed here:

$$\mathrm{d[Fe(III)]/d}t = 4k_p[\mathrm{Fe^{II}HZ}][\mathrm{O_2}] + 4k_n[\mathrm{Fe^{II}Z}][\mathrm{O_2}] \qquad (2)$$

In Eq. (2), k_p and k_n represent the rate constants of the two oxidation reactions, (3) and (4), respectively:

$$\mathrm{Fe^{II}HZ} + \mathrm{O_2} \xrightarrow{k_p} \mathrm{Fe^{III}Z} + \mathrm{HO_2} \qquad (3)$$

$$\mathrm{Fe^{II}Z} + \mathrm{O_2} \xrightarrow{k_n} \mathrm{Fe^{III}Z} + \mathrm{O_2^-} \qquad (4)$$

The first term in the right-hand side of Eq. (2) corresponds to the oxidation of the protonated chelate, and the second, to that of the normal chelate. The k_n value for the oxidation of Fe(II) in the DTPA system can be determined from the reaction rate obtained in the high pH region and the concentration of the corresponding nornal chelate at the pH where the reaction rate is obtained.*3 Thus, using this k_n value, the rate obtained at a low pH, and the concentrations of the protonated and normal chelates, the value can be obtained. For the NTA and the EDTAOH systems, the first term of Eq. (2) can be neglected, so the k_n value can be obtained simply from a comparison of the oxidation rate with the concentration of the normal chelate at a given pH.

The rate-pH curves shown in Fig. 5 (curve a) for the DTPA and in Fig. 6 (curve a') for the EDTA system were calculated by using the k_p and k_n values for the corresponding systems. The agreement between the observed rates and the calculated curves confirms that the proposed rate equation is satisfactory. Such an agreement was also observed in the other systems.

TABLE 1. RATE CONSTANTS FOR THE OXIDATION OF Fe(II) CHELATES AND THE FORMATION CONSTANTS OF Fe(II) AND Fe(III) CHELATES

Fe(II) chelate	(M^{-1} sec^{-1})	Logarithmic stability constant9)		
		$K_{\mathrm{Fe^{II}HL}}$	$K_{\mathrm{Fe^{II}L}}$	$K_{\mathrm{Fe^{III}L}}$
FeHEDTA	6.8×10^3	2.8		
FeEDTA	2.7×10^2		14.3	25.1
FeNTA	80		8.8	15.9
FeHDTPA	18	5.4		
FeDTPA	7.0		16.0	27.5
FeEDTAOH	1.0×10^2		12.2	19.8
FeEDTP	90		6.2	14.4
FeCyDTA	89		18.2	29.3

The values of the rate constants for several systems are listed in Table 1, along with the corresponding chelate formation constants for Fe(II) and Fe(III). It is interesting to note here that the rate constant for the oxidation of the normal chelate does not always increase with an increase in the corresponding formation constant of ferric chelate. This is contrary to the findings of King and Davidson for the oxidation of Fe(II)-simple anion systems.7) The oxidation reaction

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*3 The concentration of oxygen in the air-saturated solution in the pH region from 2 to 8 is estimated to be 2.4×10^{-4} M under the present experimental conditions.

9) J. Bjerrum, G. Schwarzenbach and L. G. Sillen, "Stability Constants," Chem. Soc., London (1956); A. Ringbom, "Complexation in Analytical Chemistry," John Wiely and Sons Inc., New York, N. Y. (1963).

of the protonated chelates always proceeds more rapidly than that of the corresponding normal chelates. For example, the rate constant for the oxidation reaction of the protonated Fe(II)-EDTA chelate is about thirty times greater than that of the normal chelate. This suggests that the addition of a proton to the normal chelate makes it liable to oxygen attack.

It may be suggested that the reaction mechanism for the oxidation of Fe(II) by oxygen in the presence of a chelating agent is as follows:

$$\mathrm{Fe^{2+} + HZ \rightleftharpoons Fe^{II}HZ} \qquad \text{(a)}$$

$$+\mathrm{H^+} \upharpoonleft\downharpoonright -\mathrm{H^+}$$

$$\mathrm{Fe^{2+} + Z \rightleftharpoons Fe^{II}Z} \qquad \text{(b)}$$

$$\mathrm{Fe^{II}HZ + O_2 \xrightarrow{k_p} Fe^{III}Z + HO_2} \qquad (3)$$

$$\mathrm{Fe^{II}Z + O_2 \xrightarrow{k_n} Fe^{III}Z + O_2^-} \qquad (4)$$

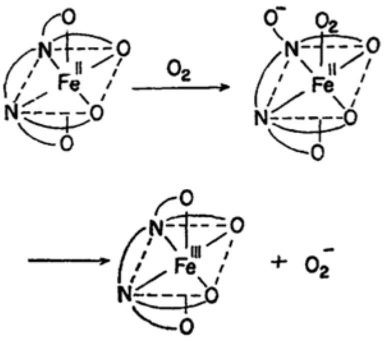
$$\mathrm{O_2^- + H^+ \rightarrow HO_2} \qquad (5)$$

$$\mathrm{Fe(II) + HO_2 + H^+ \rightarrow Fe(III) + H_2O_2} \qquad (6)$$

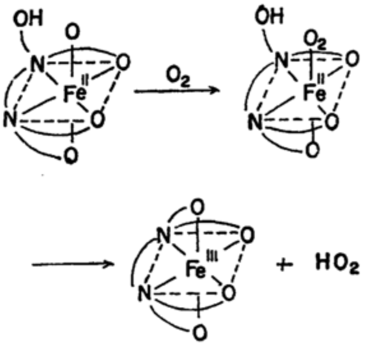
$$\mathrm{Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + OH} \qquad (7)$$

$$\mathrm{Fe(II) + OH \rightarrow Fe(III) + OH^-} \qquad (8)$$

In these equation, Fe(III) and Fe(II) represent the ferric and ferrous iron species respectively. In the reaction of Fe(II)-EDTA chelates, the mechanism of reactions (3) and (4) may be represented as follows:



(9)



(10)

The reaction (9) corresponds to Eq. (4), and the reaction (10), to Eq. (3).

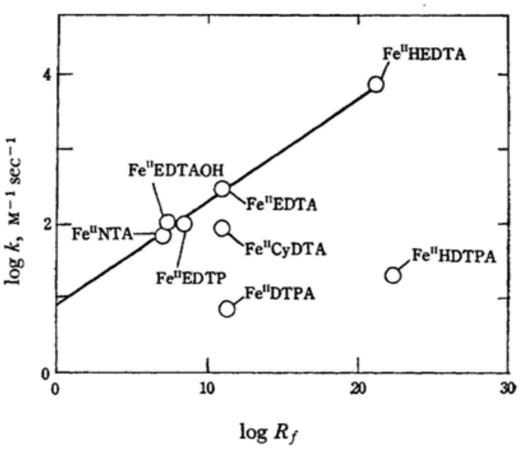


Fig. 7. Relation between $\log k$ and $\log R_f$.
k: rate constant for the oxidation of Fe(II) chelate
R_f: $K_{\mathrm{Fe^{III}L}}/K_{\mathrm{Fe^{II}L}}$*4 for normal chelate
$K_{\mathrm{Fe^{III}L}}/K_{\mathrm{Fe^{II}HL}}$*4 for protonated chelate

If the relationship between the rate constant for the oxidation of Fe(II) and the formation constants of the chelates of Fe(II) and Fe(III) are examined, in all except a few cases a straight line is obtained, as shown in Fig. 7. Thus, the experimental equation (11) can be obtained from the straight line:

$$\log k = 0.92 + 0.13 \log R_f \qquad (11)$$

Then:

$$\log k_x = 0.32 + 0.13 \log R_f \qquad (12)$$

where k_x is k_p or k_n and where k is equal to $4k_n$ and R_f, to $K_{\mathrm{Fe^{III}L}}/K_{\mathrm{Fe^{II}L}}$ in the case of the normal chelate, and where k is equal to $4k_p$ and R_f, to $K_{\mathrm{Fe^{III}L}}/K_{\mathrm{Fe^{II}HL}}$ in the case of the protonated chelate. Daviation from the straight line is observed in the CyDTA and the DTPA systems. In view of the geometrical structure of these metal chelates, the oxygen attack on them might be restricted by steric hindrance.

If the activation entropies of these reactions are assumed to be identical with each other, a relationship between $\log k$ and $\log R_f$ can be obtained, as is described below. Equation (13) is obtained on the basis of the above assumption. It represents a linear relationship between standard free energy change, ΔG_0, and the corresponding standard free energy of activation, $\Delta G_0^{\neq}$, in the reactions.

$$\Delta G_0^{\neq} = \alpha + \beta \Delta G_0 \qquad (13)$$

where α and β are the constants. The rate constant is given kinetically by the equation:

$$k_x = \frac{\boldsymbol{k}T}{\boldsymbol{h}} \exp\,(\Delta G_0^{\neq}/\boldsymbol{R}T) \qquad (14)$$

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*4 $K_{\mathrm{Fe^{III}L}}$, $K_{\mathrm{Fe^{II}L}}$ and $K_{\mathrm{Fe^{II}HL}}$ are the formation constants of normal Fe(III), normal Fe(II) and protonated Fe(II) chelates, respectively.

and the standard free energy change in the reaction is:

$$\varDelta G_0 = -FE^0 + \boldsymbol{RT}\ln R_f \qquad (15)$$

where F is the Faraday constant and E^0, the standard oxidation potential of Reaction (16):

$$\mathrm{Fe^{2+}} = \mathrm{Fe^{3+}} + \mathrm{e^-} \quad (E^0 = -0.77\,\mathrm{V})^{10)} \qquad (16)$$

Combining Eqs. (13), (14), and (15) and by rewriting the resulting equation in logarithmic form, Eq. (17) is obtained:

$$\log k_x = \log \frac{\boldsymbol{kT}}{\boldsymbol{h}} + \frac{1}{2.303\,\boldsymbol{RT}}\{\beta FE^0 - \alpha\} - \beta \log R_f \qquad (17)$$

This equation represents the linear relationship between $\log k_x$ and $\log R_f$. By combining Eqs. (12) and (17), $\alpha = 16$ kcal mol^{-1} and $\beta = -0.13$ are obtained.

For the oxidation of the chelates described here, the straight line shown in Fig. 7 can be obtained, because the activation entropies are approximately identical with each other and because there is a compensation effect[11) between the activation enthalpy, $\varDelta H^{\ddagger}$, and the activation entropy, $\varDelta S^{\ddagger}$. Therefore, the principle of a linear-free energy relation (LFER) appears in the reactions. In the cases of DTPA and CyDTA, an exception is observed, as is shown in Fig. 7. This can be explained by lowering of the oxidation rate due to steric hidrance of the oxygen attack on these chelates.

The authors wish to express their thanks to Professor Yukichi Yoshino and Professor Mutsuo Kodama for their helpful discussions of this work.

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10) W. M. Latimar, "The Oxidation Sates of the Elements and their Potentials in Aqueous Solutions," 2nd Ed., Prentice-Hall, New York N. Y. (1952).

11) R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, **1937**, 1573.