The Inner-Sphere Mechanism Interpreted by the Hydrogen Ion Effect on the Fe^{2+} Reduction Rate of Oxalato-, Malonato-, Glycolato-, and Chloro-Cobalt(III) Complexes in Aqueous Solution

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The hydrogen ion effect on the rate of the Fe^{2+} reduction of oxalato-, glycolato-, and chloro-cobalt(III) complexes was investigated kinetically. It was found that the rates of the Fe^{2+} reduction of cobalt(III) complexes such as *trans*(*N*)-Co(ox)(*β*-ala)$_2^-$, *trans*(*N*)-Co(ox)(gly)$_2^-$, *trans*(*N*)-Co(ox)(gly)(en), Co(ox)$_3^{3-}$, and *trans*-(O,Cl)-Co(Cl)(am)(dien)$^+$ (am=glycinate, *α*-alaninate or *β*-alaninate ions) increase with an increase in the hydrogen ion concentration. This result can be explained by accounting for the protonation of the oxygen atom of the carbonyl group of the nonbridging ligand. The inner-sphere mechanism can be deduced for the Fe^{2+} reductions of these complexes due to the hydrogen-ion effect. Moreover, a kinetic study of the Fe^{2+} reduction reaction of Co(Hmalo)$(NH_3)_5^{2+}$ and Co(malo)$(NH_3)_5^+$ was carried out. An inner-sphere mechanism for these reactions is proposed from an analysis of the kinetic data. Discussion of the structure of the precursor complex and of the rate determining step for the Fe^{2+} reduction reactions of cobalt(III) complexes are also made.

One of the major problems of the Fe^{2+} reduction reaction of cobalt(III) complexes is to determine whether electron-transfer reactions proceed through the inner- or outer-sphere mechanisms. It was demonstrated that the reactions of Co(Cl)$(H_2O)_5^{2+}$,[1] and Co(Cl)(Hedta)$^-$ [2] with Fe^{2+} proceed through an inner-sphere mechanism from the kinetic measurements of the formation and decay of the transient species of these reactions. Such a direct evidence of the inner-sphere mechanism for the Fe^{2+} reduction of cobalt (III) complexes has not been so often obtained due mainly to the experimental difficulty caused by the slow rate of formation of transient products of the Fe^{3+} and the possibility of subsequent substitution.

In previous kinetic studies concerning the effect of the nonbridging ligand on the Fe^{2+} reductions of oxalato-,[3] azido,[4] chloro-[5—7] and nitrilopolyamino-carboxylato[8]-cobalt(III) complexes, the present author was inclined to favor the inner-sphere mechanism.

One of the purposes of the present work is to indirectly determine the mechanism of the Fe^{2+} reductions of some oxalato-, malonato-, glycolato-, and chloro-cobalt(III) complexes due to the effect of the hydrogen ion on the electron-transfer rate. Another purpose is the investigation of the structure of the precursor complex for the Fe^{2+} reductions of some oxalato-, malonato-, and chloro-cobalt(III) complexes. The rate-determining step is also discussed.

Experimental

Preparation of Cobalt(III) Complexes. *trans*(*N*)-K[Co(ox)(gly)$_2$],[9,10] *trans*(*N*)-K[Co(ox)(*β*-ala)$_2$],[11] K_3[Co(ox)$_3$],[12] [Co(ox)$(NH_3)_4$](ClO_4),[13] [Co(Hmalo)$(NH_3)_5$]$(ClO_4)_2 \cdot 2H_2O$,[14] [Co(glyco)(en)$_2$]Cl$\cdot H_2O$,[15] *trans*(O,Cl)-[Co(Cl)(gly)(dien)](ClO_4),[16] *trans*(O,Cl)-[Co(Cl)(*α*-ala)(dien)](ClO_4),[16] and *trans*(O,Cl)-[Co(Cl)(*β*-ala)(dien)](ClO_4),[16] used as oxidants were prepared by the methods described in the references cited. The purities and identities of the complexes were ascertained by microanalysis for carbon, hydrogen, and nitrogen and by comparing the absorption spectra with those reported in the references.

Materials. The preparation of the iron(II) stock solution and the determinations of the concentrations of the iron(II), hydrogen, and perchlorate ions in this solution were carried out by the methods similar to those described in the previous paper.[5] The other reagents were G. R. grade chemicals.

Measurements of the Reaction Rate. The rates for the aquation reactions of the cobalt(III) complexes in strong acid media are negligibly small as compared with those of the Fe^{2+} reduction reactions. The Fe^{2+} reduction rates of the cobalt(III) complexes, except for Co(ox)$_3^{3-}$, were determined by the usual spectrophotometric method. The kinetic runs for Co(ox)$_3^{3-}$ were carried out by a Yanagimoto EPS-1-type stopped flow spectrophotometer under pseudo-first order conditions, the concentration of iron(II) ion being notably in excess of that of the cobalt(III) complex. The decrease in absorption was observed at a wavelength in the vicinity of the first absorption maximum of the complexes.

The concentration of the perchlorate ion in the solution was controlled by the addition of a sodium perchlorate solution. The hydrogen ion concentrations were varied from 0.05 M to 1.3 M by the addition of perchloric acid.

Results and Discussion

Figure 1 shows the dependence of the second-order rate constant on the hydrogen ion concentration for the Fe^{2+} reduction of *trans*(*N*)-Co(ox)(gly)$_2^-$ when the

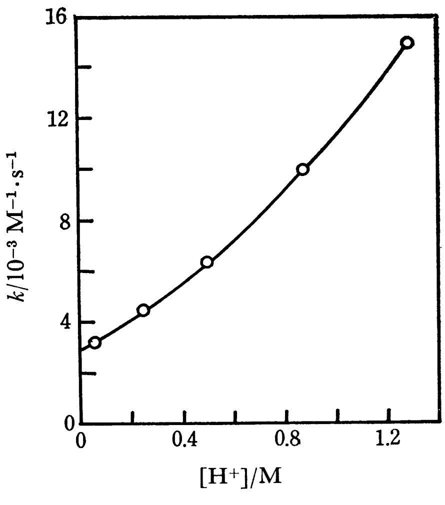

Fig. 1. The relation between the second-order rate constant of *trans*(*N*)-Co(ox)(gly)$_2^-$ and hydrogen ion concentration. $\sum[ClO_4^-]=1.30$ M, 25 °C, $NaClO_4$–$HClO_4$ medium.

ionic strength was maintained by the addition of sodium perchlorate. The second-order rate constant increases with the hydrogen-ion concentration. Similar results were obtained in the cases of *trans*-(*N*)-Co(ox)(*β*-ala)$_2^-$, Co(ox)$_3^{3-}$ (Table 1), *trans*(*N*)-Co(ox)(gly)(en) (Fig. 2), *trans*(O,Cl)-Co(Cl)(gly)(dien)$^+$ (Fig. 3), *trans*(*N*)-Co(Cl)(*β*-ala)(dien)$^+$ (Fig. 3), and *trans*(O,Cl)-Co(Cl)-(*α*-ala)(dien)$^+$. In the cases of Co(ox)(NH$_3$)$_4^+$,[17] Co-(ox)(en)$_2^+$, Co(glyco)(en)$_2^+$ (Table 1), and *cis*-Co(Cl)-(A)(en)$_2^{2+}$ (A=alkylamine),[6] however, no evidence of the hydrogen ion dependence was observed. The enhancement of the rate can be explained by the protonation of the carbonyl group of the carboxylate ion of the ligand which cannot be an electron mediator. Protonation would reduce the difficulty of stretching the ligand from the cobalt(III) center before the electron-transfer reaction takes place.

Table 1. The effect of hydrogen ions on the Fe^{2+} reduction rate of Co(ox)$_3^{3-}$ and Co(glyco)(en)$_2^+$

Complex ion	[H$^+$] / M	Rate constant / m^{-1} s^{-1}
Co(ox)$_3^{3-}$ a)	0.10	1.3×10
	0.50	2.7×10
	1.00	4.1×10
Co(glyco)(en)$_2^+$ b)	0.10	5.3×10^{-6}
	0.50	5.2×10^{-6}
	1.00	5.3×10^{-6}

a) NaClO$_4$-HClO$_4$ medium, $\sum[\mathrm{ClO_4^-}]=1.0$ M, 25 °C.
b) NaClO$_4$-HClO$_4$ medium, $\sum[\mathrm{ClO_4^-}]=1.0$ M, 25 °C.

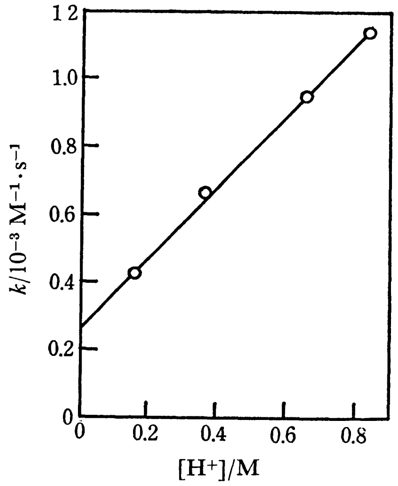

Fig. 2. The relation between the second-order rate constant of *trans*(*N*)-Co(ox)(gly)(en) and hydrogen ion concentration. $\sum[\mathrm{ClO_4^-}]=2.5$ M, 39.8 °C, NaClO$_4$-HClO$_4$ medium.

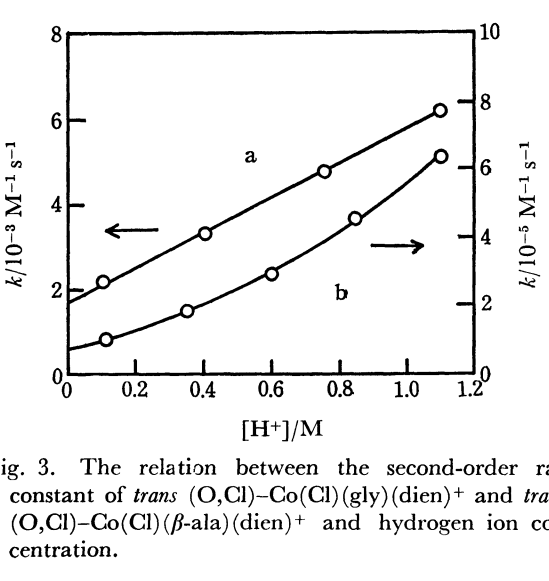

Fig. 3. The relation between the second-order rate constant of *trans* (O,Cl)–Co(Cl)(gly)(dien)$^+$ and *trans*-(O,Cl)–Co(Cl)(*β*-ala)(dien)$^+$ and hydrogen ion concentration.

Independent evidence for the protonation of the carbonyl oxygen was obtained in the kinetic study of the acid-catalyzed oxygen exchange reaction between oxalato-cobalt(III) complexes with H$_2^{18}$O.[18] Further proof of the protonation of the nonbridging ligand was also indirectly obtained in the Fe^{2+} reduction of *trans*-Co(N$_3$)$_2$(NH$_3$)$_4^+$[19] and *trans*-Co(N$_3$)$_2$(en)$_2^+$.[4] For the Fe^{2+} reduction of *trans*-Co(N$_3$)$_2$(NH$_3$)$_4^+$, the kinetic study suggested the inner-sphere mechanism. Therefore, the acid-catalyzed reduction of *trans*(O,Cl)-Co(Cl)-(am)(dien)$^+$ may suggest that the reaction proceeds through the chloride-bridged activated state. As mentioned above, the reduction rates of Co(ox)(NH$_3$)$_4^+$, Co(ox)(en)$_2^+$, and Co(glyco)(en)$_2^+$ are independent of the hydrogen ion concentration. However, for *trans*-(*N*)-Co(ox)(gly)(en) in which one of the ethylenediamine molecules in the Co(ox)(en)$_2^+$ is replaced with a glycinate ion, an acid-catalyzed enhancement of the rate is observed (Fig. 2). For this complex, the inner-sphere mechanism may be proposed. The hydrogen ion may attack the oxygen atom of the carbonyl group of the glycinate ion of *trans*(*N*)-Co(ox)(gly)(en). The possible structure of the precursor complex for the Fe^{2+} reduction of Co(ox)(NH$_3$)$_4^+$ may be represented in Fig. 4. The rate of the Fe^{2+} reduction reaction which proceeds by the formation of the precursor complex shown in Fig. 4 should be much larger than that which proceeds by the formation of the iron(II) non-chelated precursor complex.

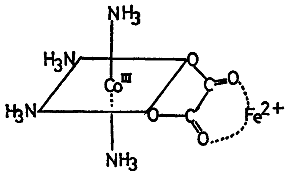

Fig. 4. The structure of the precursor complex for the Fe^{2+} reduction of Co(ox)(NH$_3$)$_4^+$.

The inner-sphere electron-transfer reaction between cobalt(III) complexes and Fe^{2+} should proceed *via* the following three steps:

$$\mathrm{RCo^{III}L} + \mathrm{Fe^{II}(H_2O)_6} \rightleftharpoons \mathrm{RCo^{III}LFe^{II}(H_2O)_{6-n}} + n\mathrm{H_2O} \tag{1}$$

$$\mathrm{RCo^{III}LFe^{II}(H_2O)_{6-n}} \rightleftharpoons \mathrm{RCo^{II}LFe^{III}(H_2O)_{6-n}} \tag{2}$$

$$\mathrm{RCo^{II}LFe^{III}(H_2O)_{6-n}} + m\mathrm{H_2O} \rightleftharpoons \mathrm{RCo^{II}(H_2O)_m} + \mathrm{LFe^{III}(H_2O)_{6-n}} \quad (\text{or } \mathrm{RCo^{II}L} + \mathrm{Fe^{III}(H_2O)_6}) \tag{3}$$

where reactions (1), (2), and (3) indicate the formation of the precursor complex, electron-transfer, and the decomposition of the successor complex, respectively.

The reaction of *trans*-$\mathrm{Co(HCO_2)(en)_2^{+}}$ [20] and *trans*-$\mathrm{Co(N_3)_2(en)_2^{+}}$ [21] with $\mathrm{V^{2+}}$ is independent of the hydrogen ion concentration, whereas the reaction of *trans*-$\mathrm{Co(HCO_2)_2(en)_2^{+}}$ with $\mathrm{Cr^{2+}}$ [22] involves an important term of first-order with respect to the hydrogen ion concentration. However, the $\mathrm{V^{2+}}$ and $\mathrm{Cr^{2+}}$ reductions of *cis*-$\mathrm{Co(HCO_2)_2(en)_2^{+}}$ do not exhibit an acid-catalyzed effect. Such a different behavior of the hydrogen ion on the *trans*-$\mathrm{Co(HCO_2)_2(en)_2^{+}}$ has been ascribed to the difference of the rate-determining steps.[22] For the $\mathrm{Cr^{2+}}$ reactions, the electron-transfer step is rate determining. This step requires a change in the inner-sphere and the electronic energy levels of the two metal centers. Protonation of the trans ligand on the oxidant appears to have the effect of facilitating such changes and lowering the energy of the acceptor orbital.[22] Therefore, the electron-transfer rate may be accelerated by the addition of a hydrogen ion. With $\mathrm{V^{2+}}$ as the reductant, the formation of the precursor complex appears to be rate-determining.[20,21]

The reactivity of the cobalt(III) complex with $\mathrm{Fe^{2+}}$, in general, is strikingly affected by the ligand coordinated to the cobalt(III) center. In a strong acid medium, the successor complex, $\mathrm{Co^{II}LFe^{III}}$ should much easily decompose because of the susceptibility of Co(II) and Fe(III) complexes to substitution and of the low stability of Co(II) complexes. The rates of the $\mathrm{Fe^{2+}}$ reduction of the oxalato- and chloro-cobalt(III) complexes are notably smaller than that of water exchange between $\mathrm{Fe(H_2O)_6^{2+}}$ and $\mathrm{H_2{}^{18}O}$.[23] Consequently, water molecule removal from the first-coordination sphere of $\mathrm{Fe(H_2O)_6^{2+}}$ in forming a bridged activated state cannot be, in general, a rate-determining step. On the basis of the acid-catalyzed rate enhancement observed in the $\mathrm{Fe^{2+}}$ reductions of oxalato- and chloro-cobalt(III) complexes, the present author is inclined to favor the electron-transfer step as the rate-determing one. With the rate-determing step being electron-transfer, reorganization of the first coordination sphere of the cobalt(III) complex would be needed before the electron-transfer reaction occurs. The previous investigation showed that the change in the reactivity of $\mathrm{Co(ox)(N_4)^{+}}$ ($\mathrm{N_4{=}(NH_3)_4, (en)_2, (trien), (phen)_2, (bpy)_2}$) with the iron(II) ion was mainly ascribed to the change in the enthalpy of activation.[3] This fact may mean that the rate-determining step is electron-transfer and that the reorganization of the first-coordination sphere of the Co(III) complex is a very important factor in the determination of the electron-transfer rate.

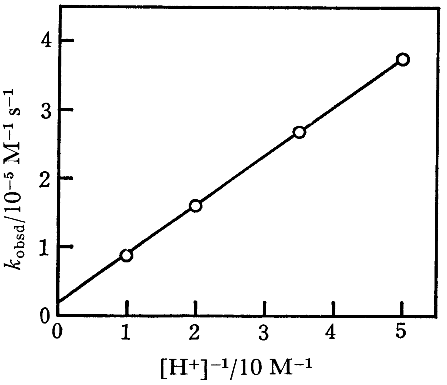

Fig. 5. The relation between the apparent second-order rate constant of $\mathrm{Co(Hmalo)(NH_5)_3^{2+}}$ and hydrogen ion concentration. $\sum[\mathrm{ClO_4^-}]=1.0$ M, 25 °C.

The acid dissociation constant for malonate ions (Hmalo), $\mathrm{Co(Hmalo)(NH_3)_5^{2+}}$, which was determined in this work, is $K_a=6.3\times10^{-4}$ M at 25 °C and $I=1.0$. In the $[\mathrm{H^+}]$ range from 0.02 M to 0.10 M, the predominant species is $\mathrm{Co(Hmalo)(NH_3)_5^{2+}}$, and the concentration of $\mathrm{Co(malo)(NH_3)_5^{+}}$ is very small. Assuming the large reactivity of $\mathrm{Co(malo)(NH_3)_5^{+}}$, the results of the kinetic study on the $\mathrm{Fe^{2+}}$ reduction conform to the reaction path shown in reaction (4).

$$\begin{tikzcd} \mathrm{Co(Hmalo)(NH_3)_5^{2+}} \arrow[r, rightleftharpoons, "K_a"] \arrow[d, "\mathrm{Fe^{2+}}"', "k_{\mathrm{H^+}}"] & \mathrm{Co(malo)(NH_3)_5^{+}} + \mathrm{H^+} \arrow[d, "\mathrm{Fe^{2+}}"', "k_0"] \\ \mathrm{Co(II)} + \mathrm{Fe(III)} & \mathrm{Co(II)} + \mathrm{Fe(III)} \end{tikzcd} \qquad (4)$$

Then, the observed rate constant k_{obsd} of the form $-\mathrm{d[Co(III)]}/\mathrm{d}t=k_{\mathrm{obsd}}[\mathrm{Co(III)}][\mathrm{Fe^{2+}}]$ can be expressed as:

$$k_{\mathrm{obsd}}=\frac{k_{\mathrm{H^+}}[\mathrm{H^+}]+k_0K_a}{[\mathrm{H^+}]+K_a} \qquad (5)$$

where $k_{\mathrm{H^+}}$ and k_0 are the second-order rate constants for $\mathrm{Co(Hmalo)(NH_3)_5^{2+}}$ and $\mathrm{Co(malo)\,(NH_3)_5^{+}}$, respectively. Under the condition that $K_a\ll[\mathrm{H^+}]$, $k_{\mathrm{H^+}}$ and k_0 can be obtained conveniently by plotting k_{obsd} *vs.* $1/[\mathrm{H^+}]$ (Fig. 5). The rate constants obtained are listed along with those for $\mathrm{Co(Hox)(NH_3)_5^{2+}}$ and $\mathrm{Co(ox)(NH_3)_5^{+}}$ in Table 2. The reactivities of $\mathrm{Co(ox)(NH_3)_5^{+}}$ and $\mathrm{Co(malo)(NH_3)_5^{+}}$ are about 10^3 times larger than

Table 2. The second-order rate constant for the iron(II) reduction of $\mathrm{Co(L)(NH_3)_5^{n+}}$ ($\mathrm{L{=}Hox^-, ox^{2-}}$ $\mathrm{Hmalo^-, malo^{2-}}$) and the p$K_a$ of $\mathrm{Co(Hox)(NH_3)_5^{2+}}$ and $\mathrm{Co(Hmalo)(NH_3)_5^{2+}}$

Complex ion	Rate constant / $\mathrm{M^{-1}\,s^{-1}}$	pK_a
$\mathrm{Co(Hox)(NH_3)_5^{2+}}$	5×10^{-4} [a]	2.06[a]
$\mathrm{Co(ox)(NH_3)_5^{+}}$	4.3×10^{-1} [a]	
$\mathrm{Co(Hmalo)(NH_3)_5^{2+}}$	1.5×10^{-6} [b]	3.2[b]
$\mathrm{Co(malo)(NH_3)_5^{+}}$	1.3×10^{-3} [b]	

a) From Ref. 24, $I=0.52$, 25 °C. b) Present work, $I=1.0$, 25 °C, in a $\mathrm{NaClO_4}$-$\mathrm{HClO_4}$ medium.

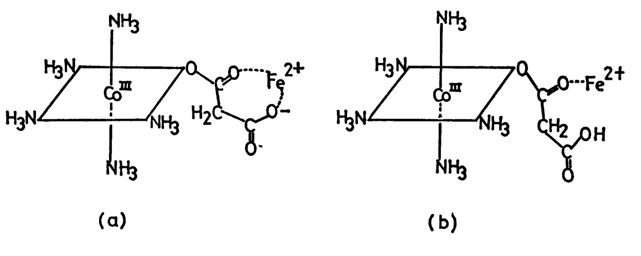

Fig. 6. The structure of the precursor complex for the $\mathrm{Fe^{2+}}$ reduction of $\mathrm{Co(Hmalo)(NH_3)_5^{2+}}$ and $\mathrm{Co(malo)\text{-}(NH_3)_5^{+}}$.

those of the corresponding protonated species (Table 2). The striking variation in the rate between the protonated species and the deprotonated species may be due mainly to the difference in the thermodynamic stability of the precursor complex, although an effect of the difference in charge on the cobalt(III) complex is not completely excluded. In the transition state for the Fe^{2+} reduction of $Co(malo)(NH_3)_5^+$, iron(II) is expected to chelate to a malonate ion(Fig. 6a). The reaction of $Co(Hmalo)(NH_3)_5^{2+}$ should proceed *via* the iron(II) non-chelated precursor complex (Fig. 6b). Moreover, the rate constants of $Co(Hox)(NH_3)_5^{2+}$ and $Co(ox)(NH_3)_5^+$ are larger by a factor of approximately 10^3 than that of the corresponding malonato-cobalt(III) complex. Possibly the difference in reactivity between the oxalato-cobalt(III) complex and the malonato-cobalt(III) complex may be related to the difference in the stabilities of the precursor complex and/or the efficiency of the bridging ligand as the electron mediator.

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