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The Kinetics of Electron-transfer Reactions between Oxalato-Cobalt(III) Complexes and Iron(II) in Acid Aqueous Solutions

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An investigation of the Fe^{2+} reductions of $Co(ox)(NH_3)_4^+$, $Co(ox)(en)_2^+$, $Co(ox)(trien)^+$, $Co(ox)(dip)_2^+$, $Co(ox)_2(en)^-$, and *cis*-$Co(ox)_2(NH_3)_2^-$ has been carried out spectrophotometrically. The rate constants of $Co(ox)N_4^+$-type complexes increase in this order: $Co(ox)(phen)_2^+ > Co(ox)(dip)_2^+ > Co(ox)(NH_3)_4^+ > Co(ox)(en)_2^+ > Co(ox)(trien)^+$, and these of $Co(ox)_2N_2^-$-type complexes, *cis*-$Co(ox)_2(NH_3)_2^- > Co(ox)_2(en)^-$. The variation in reactivity is mainly ascribed to a change in the enthalpy of activation. The rate constants of $Co(ox)(NH_3)_4^+$, $Co(ox)(en)_2^+$, *cis*-$Co(ox)_2(NH_3)_2^-$, and $Co(ox)_3^{3-}$ increase with the values of the half-wave potential of the polarographic reduction ($Co^{III} \rightarrow Co^{II}$) and with the decrease in the wave number of the maxima of the absorption spectra of the complexes.

The effect of a variation in the nonbridging ligand on the Fe^{2+} reductions of Co(III) complexes containing chloride, bromide, and azide ions as the bridging ligands has been investigated extensively[1-8] It has been demonstrated that the reactivities of *trans*-$CoN_3X(en)_2^{n+}$ ($X=H_2O$, Cl^-, N_3^-) with Fe^{2+} are affected by the free energy of activations required to stretch the *trans*-ligand of X away from the Co(III) center before electron-transfer occurs.[2]

Link found that a change in the nonbridging ligands has the same effect on the reaction of *cis*- and *trans*-$CoClY(en)_2^{2+}$ ($X=H_2O$, NH_3) with Fe^{2+} as it does on the reactions with *cis*- and *trans*-$CoBrY(en)_2^{2+}$.[8]

Recently, the kinetics of the Fe^{2+} reductions of *trans*-(O,Cl)-$CoCl(am)(dien)^+$ (am=amino acid ion and dien=diethylenetriamine) and *trans*(N)-$Co(am)_2(ox)^-$ (ox=oxalate ion) were studied. The effect of amino acids as the nonbridging ligands on the reduction rate of the former is not essentially different from that observed in the reductions of the latter.

In this connection the kinetics of the Fe^{2+} reductions of *cis*-$Co(ox)_2(NH_3)_2^-$, $Co(ox)_2(en)^-$, $Co(ox)(NH_3)_4^+$, $Co(ox)(en)_2^+$, $Co(ox)(trien)^+$, $Co(ox)(dip)_2^+$, and $Co(ox)(phen)_2^+$, (trien=triethylenetetramine, dip=2, 2′-dipyridyl, phen=1,10-phenanthroline) were studied. The correlation between the reactivity and the activation parameters, and also the half-wave potential of the polarographic reduction ($Co^{III} \rightarrow Co^{II}$) will be reported here. The effect of an unsaturated nonbridging ligand, such as 2,2′-dipyridyl or 1,10-phenanthroline, on the Fe^{2+} reduction rate of Co(III) complexes will also be discussed.

Experimental

Preparations of Co(III) Complexes. $[Co(ox)NH_3)_4]Cl$,[9] $[Co(ox)(en)_2]Cl \cdot H_2O$,[10] $[Co(ox)(trien)]Cl$,[11] $NH_4[Co(ox)_2(NH_3)_2]H_2O$,[12] $Na[Co(ox)_2(en)]$,[13] and $[Co(ox)(phen)_2]Cl \cdot 4H_2O$ were prepared by methods similar to those described in the references cited. Found: C, 9.11; H, 4.62; N, 21.94%; Calcd for $[Co(ox)(NH_3)_4]Cl$: C, 9.58; H, 4.83; N, 22.36%. Found: C, 22.55; H, 5.65; N, 16.92%; Calcd for $[Co(ox)(en)_2]Cl \cdot H_2O$: C, 22.47; H, 5.65; N, 17.47%. Found: C, 28.18; H, 5.99; N, 16.55%; Calcd for $[Co(ox)(trein)]Cl$: C, 28.89; H, 5.47; N, 16.85%. Found: C, 15.69; H, 4.01; N, 13.20%; Calcd for $NH_4[Co(ox)_2(NH_3)_2] \cdot H_2O$: C, 15.75; H, 3.97; N, 13.78%. Found: C, 22.44 H, 2.31; N, 8.79%: Calcd for $Na[Co(ox)_2(en)]$: C, 22.66; H, 2.54; N, 8.81%. Found: C, 50.84; H, 3.72; N, 9.42%: Calcd for $[Co(ox)(phen)_2]Cl \cdot 4H_2O$: C, 50.80: H, 3.90; N, 9.10%.

Preparation of $[Co(ox)(dip)_2]ClO_4$.[15] To a hot water solution (100 m*l*) containing 2.1 g of *cis*-$[CoCl_2(dip)_2]Cl$, we added 2.0 g of sodium oxalate dissolved in 50 m*l* of hot water; the mixture was then heated on a water bath (60~70°C) for 30 min. The solution was filtered, and the sodium perchlorate was added to the filtrate. The orange crystals which precipitated were filtered. The crude complex was recrystallized from hot 5 N sulfuric acid by the addition of sodium perchlorate. Found: C, 47.93; H, 2.78; N, 10.08%: Calcd for $[Co(ox)(dip)_2]ClO_4$: C, 47.29; H, 2.89; N, 10.21%.

Materials. The preparation of the iron(II) solution and the determinations of the iron(II), the sulfate ion, and the hydrogen ion were carried out by a method similar to that described in a previous paper.[3] The concentration of the sulfate ions of all the reaction mixtures except for *cis*-$Co(ox)_2(NH_3)_2^-$ and $Co(ox)_2(en)^-$ was adjusted to 1.5 M by the addition of sulfuric acid. The reductions of *cis*-$Co(ox_2)(NH_3)_2^-$ and $Co(ox)_2(en)^-$ were carried out in perchloric acid media. All the other reagents used for the preparation of the stock solutions were of a guaranteed reagent quality.

Kinetic Measurements. The cobalt(III) and the iron(II) solutions, both of which contained the necessary amount of sulfuric acid, were kept in a thermostat. The desired volume of the iron(II) solution was added to the cobalt(III) solution. The solution was then transferred into a 1-cm cell compartment of a Hitachi Model EPS-3 type recording

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15) Independent of this work, another method of preparation has already appeared; *cf.* Ref. **14**.

Table 1. Rate constants, activation parameters, and the spectral data for the oxalato-cobalt(III) complexes

Complex	Rate constant $\text{M}^{-1}\,\text{sec}^{-1}$	$\varDelta H^{\neq}$ kcal mol^{-1}	$\varDelta S^{\neq}$ eu	λ_1[c], nm	λ_2[d], nm
$Co(ox)(NH_3)_4^+$	7.45×10^{-4} [a]	16.7 ± 0.3	-16.7 ± 1.0	512	360
$Co(ox)(en)_2^+$	2.28×10^{-5} [a]	19.1 ± 0.3	-15.6 ± 1.0	500	358
$Co(ox)(trien)^+$	1.67×10^{-5} [a]	19.6 ± 0.7	-14.8 ± 2.3	496	360
$Co(ox)(dip)_2^+$	1.24 [a]	10.8 ± 0.5	-19.1 ± 1.7	500	—
$Co(ox)(phen)_2^+$	3.55 [a]	9.5 ± 0.4	-24.0 ± 1.3	508	—
$Co(ox)_2(NH_3)_2^-$	4.78×10^{-2} [b]	14.3 ± 0.5	-16.5 ± 1.7	555	386
$Co(ox)_2(en)^-$	3.67×10^{-3} [b]	16.1 ± 0.3	-15.6 ± 1.0	544	358

a) $\sum[SO_4^{2-}]=1.5\,\text{M}$, $[H_2SO_4]=0.55\,\text{M}$, 25 ± 0.1°C. b) $\sum[ClO_4^-]=1.0\,\text{M}$, $[HClO_4]=0.20\,\text{M}$, 25 ± 0.1°C, $[Fe^{2+}]=0.271\,\text{M}$.
c) Wavelength for the first absorption maxima. d) Wavelength for the second absorption maxima.

spectrophotometer.[16] The absorbance at the wavelengths corresponding to the first absorption maxima for the complexes was measured automatically. All the kinetic experiments except for that of $Co(ox)(dip)_2^+$ were run under pseudo-first order conditions with respect to $[Fe^{2+}]$. For $Co(ox)(dip)_2^+$, the rate constants were obtained under second-order conditions. The second-order rate constants were obtained by the usual method.

Results

Reductions of Co(III) Complexes. The reduction rates of all the Co(III) complexes except for *cis*-$Co(ox)_2(NH_3)_2^-$ and $Co(ox)_2(en)^-$ were first-order with respect to both the Fe^{2+} and Co(III) concentrations. Therefore, the rate equation may be represented as follows: $-d[Co(III)]/dt=k[Co(III)]\,[Fe^{2+}]$. The rate constants and the activation parameters are summarized in Table 1.

As may be seen from the kinetic data of $Co(ox)_2(en)^-$ listed in Table 2, the second-order constants increase slightly with the Fe^{2+} concentration under the conditions of constant perchlorate-ion and hydrogen-ion concentrations. Similar results were obtained in the reaction of *cis*-$Co(ox)_2(NH_3)_2^-$. The ionic strength increases with the Fe^{2+} concentration, though the perchlorate-ion concentration remains constant (Table 2). The increase in the ionic strength must be one of the reasons for the increase in the second-order rate constant with the Fe^{2+} concentration. No further experiments were carried out in order to investigate the effect of the Fe^{2+} concentration on the reduction rate.

Table 2. The kinetic data for the Fe^{2+} reductions of $Coox_2(en)^-$ under the conditions of $[H^+]=0.50\,\text{M}$, 25 ± 0.1°C and $\sum[ClO_4^-]=2.0\,\text{M}$.[a]

Fe(II), M	Ionic-strength	Rate constant, $\text{M}^{-1}\,\text{sec}^{-1}$
0.136	2.14	3.60×10^{-3}
0.271	2.27	4.08×10^{-3}
0.407	2.41	4.58×10^{-3}
0.541	2.54	4.83×10^{-3}
0.679	2.69	5.50×10^{-3}

a) The perchlorate ion concentration was adjusted by the addition of lithium perchlorate.

The activation parameters for *cis*-$Co(ox)_2(NH_3)_2^-$ and $Co(ox)_2(en)^-$ were obtained from the temperature dependence of the rates, which were obtained under the conditions of a constant Fe^{2+} concentration (Table 1).

Discussion

An oxalate-bridged mechanism was demonstrated for the Fe^{2+} reductions of $Co(ox)_3^{3-}$ and $Coox(H_2O)(NH_3)_3^+$[17] by observing the spectrum of the Fe(III) product and by determining its rate of formation. Therefore, the present author thinks that all the reactions occur *via* similar mechanisms.

The relative reactivity for the Fe^{2+} reductions of $Co(ox)(NH_3)_4^+$ and *cis*-$Co(ox)_2(NH_3)_2^-$ decreased upon the replacement of the ammonia molecules with ethylenediamine and triethylenetetramine molecules (Table 1). A similar chelate effect was also observed in Fe^{2+} reductions of $CoCl_2N_4^+$ and $CoCl(H_2O)N_4^{2+}$ ($N=(NH_3)_4$, $(en)_2$ and trien).[3] It was demonstrated that the reactivity of chloro-cobalt(III) with Fe^{2+} is affected by the effects of a) and b) : a) the ligand-field strength of the *trans*-ligand,[1,18,19] and b) the energy required to stretch the *trans*-ligand away from the Co(III) center. The rate constants of $Co(ox)N_4^+$-type complexes (N=saturated ligand) increase with a decrease in the wavenumber of the first absorption band of the complexes.

It is of interest to note here that the reactivities of $Co(ox)N_4^+$-type complexes ($N=(NH_3)_4$, $(en)_2$, trien, $(dip)_2$, $(phen)_2$) and $Co(ox)_2N_2^-$-type complexes ($N=(NH_3)_2$, and (en)) decreases remarkably with an increase in the enthalpy of activation, and that there is a certain degree of compensation effect between $\varDelta H^{\neq}$ and $T\varDelta S^{\neq}$ for the Fe^{2+} reductions of these complexes (Table 1). Figure 1 shows the good linearity between the logarithm of the rate constant and the enthalpy of activation of $Co(ox)N_4^+$-type complexes. This illustrates that the variation in reactivity is mainly due to the change in the enthalpy of activation.

The reactivity of $Co(ox)(dip)_2^+$ and $Co(ox)(phen)_2^+$ is

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[16] A 10-cm cell was used for the reaction of $Co(ox)(phen)_2^+$, because the solubility of this complex into sulfuric acid is small.

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TABLE 3. THE RATE CONSTANTS, SPECTRAL DATA AND THE HALF-WAVE POTENTIALS OF THE POLAROGRAPHIC REDUCTION ($Co^{III} \rightarrow Co^{II}$) FOR THE OXALATO-Co(III) COMPLEXES

Complex	Rate constant $M^{-1} sec^{-1}$	λ_1[d], nm	λ_2[e], nm	Half-wave potential[f] (V *vs.* S.C.E.)
$Coox(en)_2^+$	2.28×10^{-5} [a]	500	358	−0.32
$Coox(NH_3)_4^+$	7.45×10^{-4} [b]	512	360	−0.21
$Coox_2(NH_3)_2^-$	7.24×10^{-2} [b]	555	375	−0.03
$Co(ox)_3^{3-}$	$(3.3\ \pm0.1)\times10$ [c]	600	424	+

a) Present work, $\sum[SO_4^{2-}]=1.5$ M, $[H_2SO_4]=0.55$ M, 25±0.1°C, $[Fe^{2+}]=0.35$ M. b) $\sum[SO_4^{2-}]=1.5$ M, $[H_2SO_4]=0.55$ M, 25±0.1°C, $[Fe^{2+}]=0.35$ M. c) Ref. 16, $\sum[ClO_4^-[=1.0$ M, 25±0.1°C. d) Wavelength for the first absorption maxima. e) Wavelength for the second absorption maxima. f) From Ref. 20.

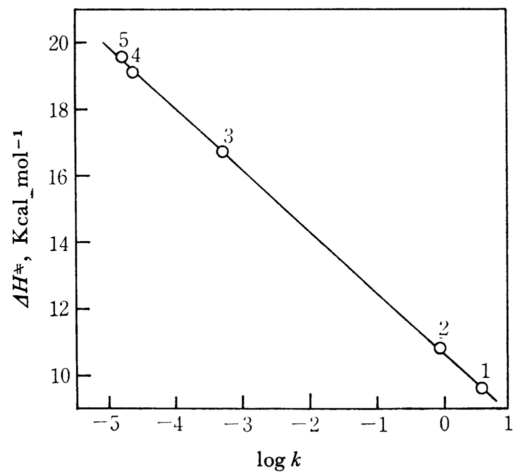

Fig. 1. Relation between the enthalpy of activation and logarithm of the rate constant for the Fe^{2+} reductions of $Co(ox)N_4^+$-type complexes.
1): $Co(ox)(phen)_2^+$, 2): $Co(ox)(dip)_2^+$, 3): $Co(ox)(NH_3)_4^+$, 4): $Co(ox)(en)_2^+$, 5): $Co(ox)(trien)^+$.
$\sum[SO_4^{2-}]=1.5$ M, $[H_2SO_4]=0.55$ M, 25±0.1°C.

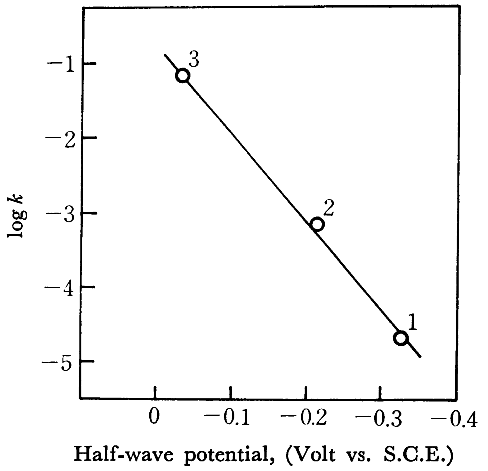

Fig. 2. Relation between the logarithm of the rate constant for the Fe^{2+} reductions of oxalato-Co(III) complexes and the half-wave potential of the polarographic reduction wave ($Co^{III}\rightarrow Co^{II}$).
1): $Co(ox)(en)_2^+$, 2): $Co(ox)(NH_3)_4^+$, 3): *cis*-$Co(ox)_2(NH_3)_2^-$, $\sum[SO_4^{2-}]=1.5$ M, $[H_2SO_4]=0.55$ M, 25±0.1°C.

very much larger than that of $Co(ox)(en)_2^+$. The larger reactivity of the former must result from the following factors: a) the efficiency of the mediators for the electron-transfer increases by the coordination of 2,2′-dipyridyl and 1,10-phenanthroline to the Co(III) ion, b) the oxidation-reduction potentials of $Co(ox)(dip)_2^+$, and $Co(ox)(phen)_2^+$ are very different from that of $Co(ox)(en)_2^+$, and c) the free energy of activation required to remove 2,2′-dipyridyl and 1,10-phenanthroline from the Co(III) center is smaller than that of ethylenediamine. However, no further, more detailed discussion could be made on the basis of the present limited kinetic data.

The rate constants of $Co(ox)_{3-n}(NH_3)_{2n}^{(3-2n)+}$ ($n=$ 0, 1, 2) shown in Table 3 increase with the number of oxatate ion coordinated to Co(III). It is also of interest that the reactivity of $Co(ox)_{3-n}(NH_3)_2^{(3-2n)+}$ with Fe^{2+} increases with the decrease in the wavenumber of the first absorption band of the complexes.

It can be seen from Table 3 that the reactivities of $Co(ox)(NH_3)_4^+$, $Co(ox)(en)_2^+$, *cis*-$Co(ox)_2(NH_3)_2^-$, and $Co(ox)_3^{3-}$ with Fe^{2+} increases with the values of the half-wave potential of the polarographic reduction ($Co^{III}\rightarrow Co^{II}$). It has already been demonstrated that there is a relation between the half-wave potentials of polarographic reduction waves and the wavenumbers of the maxima of the absorption spectra of Co(III)-oxalato complexes.[20] The relation between the values of the half-wave potential and the logarithm of the rate constants is shown in Fig. 2. This linear behavior suggests that the reduction potential ($Co^{III}\rightarrow Co^{II}$) affects the reactivity of complexes with Fe^{2+}. No attempt was made to explain quantitatively the relation between the reactivity of complexes and the half-wave potential because of the present lack of much kinetic data.

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