December, 1971] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 3367—3369 (1971) 3367

Electron-Transfer Reactions of Multidentate-ligand Cobalt(III) Complexes. III. The Reductions of Several Chloro- and Bromo(nitrilopolycarboxylato)-cobaltate(III) Ions by Iron(II)

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(Received April 16, 1971)

The reductions of chloro- and bromo(ethylenediaminetriacetatoacetic acid)cobaltate(III), chloro- and bromo(*N*-hydroxyethylethylenediamine-*N*,*N'*,*N'*-triacetato)cobaltate(III), and dichloro(ethylenediaminediacetato)cobaltate(III) ions by iron(II) in perchloric acid solutions obey the second-order rate expression: $-\mathrm{d}[\mathrm{Co(III)}]/\mathrm{d}t = k_c[\mathrm{Co(III)}][\mathrm{Fe}^{2+}]$. The second-order rate constants, k_c, and activation parameters for these reactions were determined spectrophotometrically. For the cases of all the Co(III) complexes investigated, an increase in the rate constant with the hydrogen-ion concentration at a constant ionic strength is expressed by: $\log k_c = \log k_0 + A[\mathrm{H}^+]$, where k_0 and A are constants for the given complex at a constant ionic strength and temperature. The hydrogen-ion dependence can be explained by the difference in the degree of stabilization of the Co(III) anion between that by hydrogen ions and that by sodium ions.

In previous papers, the results of kinetic studies of the electron-transfer reactions of the cobalt(III) complexes of the $\mathrm{CoN_4Cl_2}^+$, $\mathrm{CoN_4OH_2Cl}^{2+}$ 1) ($\mathrm{N_4} = (\mathrm{NH_3})_4$, $(\mathrm{en})_2$, and trien2)) and $\mathrm{CoN_5Cl}^{2+}$ 3) ($\mathrm{N_5} = (\mathrm{NH_3})_5$ and tetren4)) types have been reported. In these studies, the effect of nonbridging ligands on the electron-transfer process were of major interest.

Haim and Sutin5) found that iron(II) reductions of $\mathrm{Co(HY)Cl}^-$ (Y^{4-}=ethylenediaminetetraacetate) proceeds by means of a chloride-bridged inner-sphere mechanism. The behavior of the reaction of $\mathrm{Co(HY)Cl}^-$ with iron(II) has also been investigated by Pidcock and Higginson.6) No kinetic studies of the other monohalogeno- and dihalogeno(nitrilopolycarboxylato)cobaltate(III) complexes have been published, however; the present work on the reaction kinetics was undertaken in order to establish the features of the reaction mechanism.

Experimental

Materials. The stock solution of iron(II) perchlorate was prepared by dissolving iron wire (Mallinckrodt Co. Anala R quality) in a dilute perchloric acid solution. The concentrations of the iron(II), perchrolate, and hydrogen ions were determined by methods similar to those previously reported.1) All the other reagents used for the preparation of the stock solutions were of a guaranteed reagent quality. Redistilled water was used for the preparation of the reaction mixture.

Preparations of Cobalt(III) Complexes. Sodium chloro- and bromo(ethylenediaminetriacetatoacetic acid)cobaltate(III) (Na[Co(H·EDTA)Cl]7) and Na[Co(H·EDTA) Br]8)), sodium chloro- and bromo(*N*-hydroxyethylethylenediamine *N*,*N'*,*N'*-triacetato)cobaltate(III) (Na[Co(EDTAOH)Cl],7) and Na[Co(EDTAOH)Br]8)) were prepared by methods similar to those described in the references cited.

Found: C, 28.76; H, 3.82; N, 6.36%. Calcd for Na[Co(H·EDTA)Cl]·$0.5\mathrm{H_2O}$: C, 28.90; H, 3.40; N, 6.74%.

Found: C, 25.29; H, 3.57; N, 5.83%. Calcd for Na[Co(H·EDTA)Br]·$\mathrm{H_2O}$: C, 25.61; H, 3.22; N, 5.97%.

Found: C, 28.59; H, 4.41; N, 6.46%. Calcd for Na[Co(EDTAOH)Cl]·$1.5\mathrm{H_2O}$: C, 28.62; H, 4.32; N, 6.68%.

Found: C, 27.74; H, 4.35; N, 6.29%. Calcd for Na[Co(EDTAOH)Br]·$\mathrm{H_2O}$: C, 26.39; H, 3.77; N, 6.16%.

Sodium dichloro(ethylenediaminediacetato)cobaltate(III). $\mathrm{CoCl_2 \cdot 6H_2O}$ (4.6 g) and ethylenediaminediacetic acid (3.6 g) were dissolved in 100 m*l* of water. A sodium hydroxide solution (1.6 g in 50 m*l* of water) was then added to the solution, and the Co(II) was oxidized by the addition of 20 m*l* of a 30% hydrogen peroxide solution. Dark blue crystals were obtained after the addition of 100 m*l* of concentrated hydrochloric acid; they were recrystallized from alcohol-water.

Found: C, 22.31; H, 3.49; N, 8.97%. Calcd for Na[Co(EDDA)$\mathrm{Cl_2}$]: C, 22.04; H, 3.08; N, 8.57%.

The electronic spectral data for the complexes are included in Table 1.

TABLE 1. SPECTRAL DATA FOR COBALT(III) COMPLEXES

Complex	$\lambda_{\max}$ a) nm	$\varepsilon_{\max}$
Na[Co(H·EDTA)Cl]	583	225
Na[Co(H·EDTA)Br]	594	223
Na[Co(EDTAOH)Cl]	583	207
Na[Co(EDTAOH)Br]	593	210
Na[Co(EDDA)$\mathrm{Cl_2}$]	599	246

a) First absorption maximum.

Kinetic Measurements. The cobalt(III) and iron(II) solutions, both of which contained the necessary amounts of perchloric acid and sodium perchlorate, were kept in a thermostat. The desired volume of the iron(II) solution was then added to the cobalt(III) solution, the solution was transferred to a 1-cm cell which had been placed in a thermostated cell compartment of a Hitachi Model 125 Recording Spectrophotometer, and the absorbance of the reaction mixture in the vicinity of the absorption maximum for the cobalt(III) complex was recorded as a function of the time. Most of the experiments were carried out under second-order conditions. The second-order rate constants,

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1) Y. Kurimura, K. Ohashi, T. Ohtsuki, and K. Yamamoto, This Bulletin, **44**, 1293 (1971).

2) en=ethylenediamine and trien=triethylenetetramine.

3) Y. Kurimura and K. Ohashi, This Bulletin, **44**, 1797 (1971).

4) tetren=tetraethylenepentamine.

5) A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **88**, 5343 (1966).

6) A. Pidcock and W. C. Higginson, *J. Chem. Soc.*, **1963**, 2798.

7) M. L. Morris and D. H. Busch, *J. Amer. Chem. Soc.*, **78**, 5179 (1956).

8) G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

k_c, for each run were evaluated from the slopes of the usual second-order plots. Some of the Co(EDTAOH)Br$^-$ kinetic runs were carried out under pseudo-first-order conditions. The pseudo-first-order rate constants, k_n, were evaluated from the slopes of the log (A_t-A_∞) *vs.* time plots, where A is the absorbance at time t, and A_∞, the absorbance after all the Co(III) has been reduced to Co(II). The second-order rate constant, k_c, was calculated from the equation $k_c=k_n/[\mathrm{Fe}^{2+}]$. For the cases of all the cobalt(III) complexes, the rates of the aquations of the complexes could be neglected as compared to those of the reductions.

Results

Rate Studies at a Given Hydrogen Ion Concentration. In all the cases investigated, the reductions of the Co(III) complexes by iron(II) followed the rate law of $-d[\mathrm{Co(III)}]/dt=k_c[\mathrm{Co(III)}][\mathrm{Fe}^{2+}]$, good second-order plots being obtained in up to 80—95% of the reactions. In addition, all the values of k_c were essentially constants for he given cobalt(III) complex in the region of initial concentrations of iron(II) from 0.0462 to 0.0982 M at a particular hydrogen ion concentration and ionic strength. The second-order rate constants at $[\mathrm{H}^+]=0.10$ M and $\sum[\mathrm{ClO_4}^-]=1.0$ M and at 25°C are summarized in Table 2, along with the activation parameters, which were obtained from temperature dependence of the k_c.

TABLE 2. SECOND-ORDER RATE CONSTANTS[a] AND ACTIVATION PARAMETERS[a] FOR THE REDUCTIONS OF CoZCl$^-$ [b] BY Fe^{2+}

Complex	k_c M^{-1}sec^{-1}	$\Delta H^{\neq}$ kcal mol^{-1}	$\Delta S^{\neq}$, cu
Co(H·EDTA)Cl$^-$	1.52[c]	7.8	−31
Co(H·EDTA)Br$^-$	1.23	7.0	−35
Co(EDTAOH)Cl$^-$	1.65	7.5	−33
Co(EDTAOH)Br$^-$	0.73	6.3	−38
Co(EDDA)Cl$_2$$^-$	2.36	11	−20

a) Evaluated at $[\mathrm{H}^+]=0.10$ M and $\sum[\mathrm{ClO_4}^-]=1.0$ M and at 25°±0.1°C in $\mathrm{HClO_4}$-$\mathrm{NaClO_4}$ mediums.

b) Z=H·EDTA^{3-}, EDTAOH^{3-} and EDDACl^{3-}.

c) Rate constant obtained by A. Haim and N. Sutin[5] is 1.9±0.2 M^{-1}sec^{-1} at 25°C, $\sum[\mathrm{HClO_4}]=2.2$—2.8 M and ionic strength of 3.0 M.

Dependence of the Rate Constant on the Hydrogen-ion Concentration. The hydrogen-ion dependence of the rate constant was examined in the $\mathrm{HClO_4}$–$\mathrm{NaClO_4}$ medium, in which the ionic strength was maintained at 1.0 M. The values of k_c are slightly increased with an increase in the hydrogen-ion concentration in all cases. The values of the second-order rate constants were found to vary with the hydrogen-ion concentration according to the equation:

$$\log k_c = \log k_0 + A[\mathrm{H}^+] \qquad (1)$$

where k_0 and A are constants for a given complex and at a constant ionic strength and temperature. The values of log k_c are plotted as a function of the hydrogen-ion concentration in Fig. 1. The k_0 and A values could be obtained from the intercept and slope of the log k_c *vs.* $[\mathrm{H}^+]$ plot respectively. These values are summarized in Table 3.

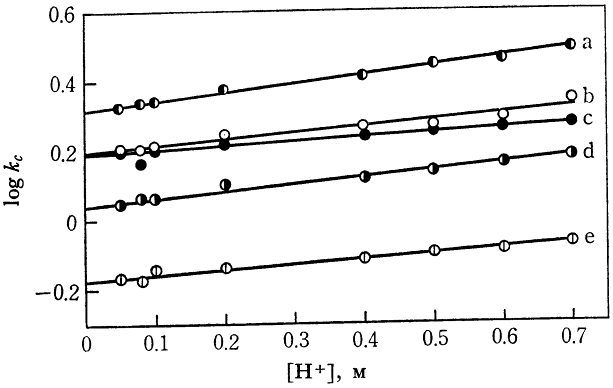

Fig. 1. Dependence of the second-order rate constant upon hydrogen ion concentration.
a : Co(EDDA)Cl$_2$$^-$ b : Co(EDTAOH)Cl$^-$
c : Co(H·EDTA)Cl$^-$ d : Co(H·EDTA)Br$^-$
e : Co(EDTAOH)Br$^-$
$[\mathrm{Fe}^{2+}]=9.73\times10^{-3}$ M, $\sum[\mathrm{ClO_4}^-]=1.0$ M, [Co(III)]= 2.44×10^{-3}—4.01×10^{-3} M, 25±0.1°C.

TABLE 3. THE VALUES OF k_0 AND A FOR THE Fe^{2+} REDUCTIONS OF CoZX$^-$ AT 25°C[a]

Complex	k_0, M^{-1}sec^{-1}	A, M^{-2}sec^{-1}
Co(H·EDTA)Cl$^-$	1.54	0.12
Co(H·EDTA)Br$^-$	1.20	0.14
Co(EDTAOH)Cl$^-$	1.57	0.18
Co(EDTAOH)Br$^-$	0.71	0.15
Co(EDDA)Cl$_2$$^-$	2.07	0.24

a) Evaluated at $\sum[\mathrm{ClO_4}^-]=1.0$ M in $\mathrm{HClO_4}$—$\mathrm{NaClO_4}$ medium and at 25±0.1°C.

Discussion

It has been demonstrated from a direct observation of the transient species of the primary product that the reaction of Co(H·EDTA)Cl$^-$ with Fe^{2+} proceeds *via* a chloride-bridged transition state.[5] Therefore, it is reasonable to assume that the reactions of CoZCl$^-$ (Z=H·EDTA^{3-}, EDTAOH^{3-}, and EDDACl^{3-}) and perhaps CoZBr$^-$ with iron(II) proceed *via* the chloride- and bromide-bridged mechanisms respectively. Such an inner-sphere reaction may be regarded as proceeding through the formation of a bridged activated complex such as $[\mathrm{Co^{III}Z\cdots Cl\cdots Fe^{II}}]$.[5] The initial products of the Co(II) and Fe(III) may be the Co(II)-aminopolycarboxylic acid complex and FeCl^{2+} [5] respectively; these substances are unstable and rapidly form Co^{2+} and the Fe(III)-aminopolycarboxylic acid complex respectively under the conditions employed.

The similar effectiveness for the Co(H·EDTA)Cl$^-$ and Co(EDTAOH)Cl$^-$ complexes, and also that for the Co(H·EDTA)Br$^-$ and Co(EDTAOH)Br$^-$ complexes, seem to suggest that there is no appreciable change in the relative effectiveness by replacing the protonated carboxyl group in the Co(H·EDTA)X$^-$ (X=Cl$^-$ and Br$^-$) complex by a $-\mathrm{CH_2OH}$ group. The Co(H·EDTA)Br$^-$ and Co(EDTAOH)Br$^-$ complexes are less reactive than the respective corresponding chloride complexes. The smaller effectiveness for the Co(III)-bromo complex compared with that of the corresponding Co(III)-chloro complex has been known in the reductions of the Co(III) complexes by low reactive reducing agents, such as Fe(II)[9,10] and Eu(II).[11,12] The bridging efficiency seems to depend primarily upon the nature of the reducing agent. This may indicate that the stabilization of the transition state by bond making to the reductants may be of greater importance than bond breaking for the reductants in the reactions investigated.[12]

The higher reactivity for the Co(EDDA)Cl_2^- complex relative to the other complexes investigated may be due to existence of two chloride ions in this complex.

A rate dependence on the hydrogen-ion concentration similar to that expressed by Eq. (1) has been proposed by Pidcock and Higginson,[6] and also there is much experimental evidence for such hydrogen-ion dependence.[6] They ascribed the relatively small increase in the rate constant with an increase in the hydrogen-ion concentration at a constant ionic strength in the iron(II) reduction of Co(H·EDTA)-Cl^- to a specific salt effect due to interaction between ions of opposite charges, rather than to a catalysis involving a reaction path in which a proton enters into the transition complex.[6] It was suggested that the increase in the second-order rate constant for the reactions of the Co(HY)Cl^- complex with iron(II) could be ascribed to a greater stabilization of the Co-(HY)Cl^- complex by sodium ions than by hydrogen ions.[6]

This explanation seems to applicable to the iron-(II) reductions of the Co(H·EDTA)Br^-, Co(EDTA-OH)Cl^-, Co(EDTAOH)Br^-, and Co(EDDA)Cl_2^- complexes since all the k_c values for these complexes followed Equation (1) rather than the first-order dependence of the hydrogen ion.

Since the uncoordinated carboxyl group in the Co(H·EDTA)X^- complex are almost all protonated under the conditions employed, and since there is no uncoordinated carboxyl group in the Co(EDTA-OH)X^- and Co(EDDA)Cl_2^- complexes, it could hardly be supposed that the reactions of these complexes proceed through a reaction path in which a proton enters into the transition state. On the other hand, there can be no rate dependence upon the hydrogen-ion concentration in the iron(II) reductions of the Co(III) complexes with positive charges, such as Co-N_5Cl^{2+} and $CoN_4Cl_2^+$ ($N_5=(NH_3)_5$, $(en)_2NH_3$, and tetren and $N_4=(NH_3)_4$, $(en)_2$, and trien[13]), in the $HClO_4$–$NaClO_4$ medium under conditions of a constant ionic strength and a relatively high hydrogen-ion concentration, because no change in the interactions between the ions of opposite charges, the Co-(III) ion and the perchlorate ion, would result from replacing the sodium ions by hydrogen ions.

The values of A, which may be a measure of the difference in the interactions between the cations (H^+ and Na^+) and the reactant Co(III) anion, are almost the same in the cases of the Co(H·EDTA)Cl^-, Co-(H·EDTA)Br^-, Co(EDTAOH)Cl^- and Co(EDTA-OH)Br^- complexes, but it is slightly larger for the case of Co(EDDA)Cl_2^-. This seems to be ascribable to the greater difference between the degree of the stabilization of this complex by sodium ions and that by hydrogen ions as compared to those of the other Co(III) complexes investigated. The relatively higher values of k_0, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and A for the Co(EDDA)Cl_2^- may suggest a somewhat different reaction pattern relative to that of the other complexes, for instance, a reaction path including a double chloride-bridged activated complex.

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[9] H. Diebler and H. Taube, *Inorg. Chem.*, **4**, 1029 (1965).

[10] J. H. Espenson, *ibid.*, **4**, 121 (1965).

[11] J. P. Candlin, J. Halpern, and D. L. Trim, *J. Amer. Chem. Soc.*, **86**, 1010 (1964).

[12] A. G. Sykes, *Adv. Inorg. Chem. Radiochem.*, **10**, 153 (1967).

[14] It seems reasonable to assume that these reactions proceed *via* the chloride-bridged activated complexes.[1,2]