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Reductions of Cobalt(III) Complexes by Iron(II) Chelates. I. The Kinetics and Mechanisms of the Reductions of Acidopentaamminecobalt(III) Complex Ions by Iron(II) Chelates of Nitrilopolycarboxylic Acids

Yoshimi Kurimura

Chemical Laboratory, College of General Education, Ibaraki University, Mito 310

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Kinetic studies have been made of the reactions of FeEDTA^{2-} with complex ions of the Co(NH$_3$)$_5$X^{2+} (X= F$^-$, Cl$^-$, Br$^-$, I$^-$, NO$_3$$^-$, NCS$^-$, and N$_3$$^-$) type. The pattern of reactivity suggests that FeEDTA^{2-} reacts with Co(NH$_3$)$_5$X^{2+} mainly through an innersphere mechanism. The variation in the rate of the reactions of Fe$^{\mathrm{II}}$Z$_m$$^-$ (Z=EDTA, CyDTA, EDTA-OH, and DTPA), in which the Z ligand is varied, with Co(NH$_3$)$_5$Cl^{2+} can be explained in terms of the steric effect, the charge effect, and the stabilization effect.

The ferrous-ion reductions of cobalt(III) complexes of several types have been investigated. However, rate studies of only a relatively small number of redox reactions between iron(II)–nitrilopolycarboxylate complex ions and metal complex ions have been reported. The reactions of FeEDTA^{2-}–MnCyDTA$^-$,[1,2] FeEDTA^{2-}–FeCyDTA$^-$,[1] and CrEDTA^{2-}–FeEDTA$^-$ [3] are known to be rapid reactions, and the reductions of Co(III)-chelate by Fe(II)-chelates such as FePDTA^{2-}–CoEDTA$^-$ [3] and FePDTA^{2-}–CoCyDTA$^-$,[3] to be relatively slow reaction. All of the above reactions seem to proceed *via* the outer-sphere activated states.[1,3] On the other hand, the inner-sphere nature of the reactions was suggested in the FePDTA^{2-} reductions of RX^{2+} (R=Co(NH$_3$)$_5$, X=Cl$^-$, Br$^-$, N$_3$$^-$, and NCS$^-$).[3]

The pattern of reactivity for the reduction of RX^{2+} by several reducing agents has been studied: the dependence of the rate for the reductions of RX^{2+} by a given reductant would give information about whether the mechanism of the electron-transfer reaction is of outer- or inner-sphere type, though it is a less direct manner.

This article will describe our investigations of the kinetics of the Fe$^{\mathrm{II}}$EDTA reductions of RX^{2+} and the Fe$^{\mathrm{II}}$Z (Z=EDTA, CyDTA, EDTA-OH, and DTPA) reductions of RCl^{2+}. The observed rate data will be explained in terms of the effects of the charge, the steric hindrance of Fe$^{\mathrm{II}}$Z, and the free energy change from the ferrous to the ferric chelate.

Experimental

Materials. The cobalt(III) complexes of the perchlorate form, [RF](ClO$_4$)$_2$,[5] [RCl](ClO$_4$)$_2$,[6] [RBr](ClO$_4$)$_2$,[7] [RI](ClO$_4$)$_2$,[8] [RNO$_3$](ClO$_4$)$_2$,[6] [RNCS](ClO$_4$)$_2$,[9] and [RN$_3$](ClO$_4$)$_2$[10] were prepared according to the published procedures. The identity and purity of the cobalt(III) products were confirmed analytically and spectrophotometrically. The wavelengths and molar absorption coefficients of the first absorption maximum of the cobalt(III) complexes prepared are summarized in Table 1.

Table 1. Spectral data (R=Co(NH$_3$)$_5$)

Complex	$\lambda_{\max}$$^{a),b)}$nm	$\varepsilon_{\max}$$^{b)}$
[RF](ClO$_4$)$_2$	509 (510)	44 (44)
[RCl](ClO$_4$)$_2$	531 (533)	49 (49)
[RBr] (ClO$_4$)$_2$	549 (550)	55 (53)
[RI](ClO$_4$)$_2$	582 (580)	82 (80)
[RNO$_3$](ClO$_4$)$_2$	501 (500)	58 (57)
[RNCS](ClO$_4$)$_2$	496 (497)	191 (192)
[RN$_3$](ClO$_4$)$_2$	518 (520)	260 (265)

a) Wavelength for first absorption maximum.

b) Values in parentheses are from the literature.[4]

The preparation of the ferrous perchlorate solution and the determinations of the concentrations of hydrogen and perchlorate ions in the solution were carried out by methods similar to those described previously.[11] The disodium salts of the ethylenediaminetetraacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethylethylenediaminetriacetic acid, and diethylenetriaminepentaacetic acid used were Dotite reagents and were used without further purification. The ferrous chelate solutions were prepared by mixing a deaerated solution of ferrous perchlorate and a slight excess of a deaerated solution of a chelating agent which had been prepared by neutralizing a solution of the chelating agent with a dilute sodium hydroxide solution. The solutions of the cobalt(III) complexes were prepared by dissolving weighed amounts of a cobalt(III) complex into an acetate buffered solution. The ionic strength of the reaction mixture was maintained at 0.50 by the addition of sodium perchlorate. All the reactant solutions were prepared under a nitrogen atmosphere. For all the reactions except for RNCS^{2+} it was necessary to use a stopped-flow technique. The spectrophotometers used

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[1] R. G. Wilkins and R. E. Yelin, *Inorg. Chem.*, **7**, 2667 (1968).

[2] The abreviation for the chelating agents used here are: EDTA, ethylenediaminetetraacetic acid; CyDTA; cyclohexanediaminetetraacetic acid; PDTA; propylenediaminetetraacetic acid; EDTA-OH; hydroxyethylethylenediaminetriacetic acid; DTPA, diethylenetriaminepentaacetic acid.

[3] B. Grossman and R. G. Wilkins, *J. Amer. Chem. Soc.*, **89**, 4230 (1967).

[4] J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86**, 1019 (1964).

[5] F. Basolo and R. K. Murmann, "Inorganic Syntheses," Vol. 4, P. 171 (1953).

[6] W. A. Hynes, L. K. Yanowski, and M. Shuller, *J. Amer. Chem. Soc.*, **60**, 3053 (1938).

[7] H. Diehl, H. Clark, and H.H. Willards, "Inorganic Syntheses," Vol. 1, P. 186 (1939).

[8] A. Haim and H. Taube, *J. Amer. Chem. Soc.*, **85**, 495 (1963).

[9] A. Werner and H. Muller, *Z. Anorg. Chem.*, **22**, 102 (1900).

[10] M. Linhard and H. Flygare, *Z. Anorg. Allgem. Chem.*, **262**, 328 (1950).

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

were a Yanagimoto Model SPS-1 stopped-flow apparatus and a Hitachi Model 124 recording spectrophotometer. The reactions were followed under pseudo-first-order conditions in which the concentration of the ferrous chelate was at least 10 times greater than that of the Co(III) complex. The reactions were monitored by following the variation in the absorbance of the reaction mixture in the vicinity of the first absorption maximum of the Co(III) complex. The pH value of the solution was measured by means of a Hitachi-Horiba F-5 type pH meter. The hydrogen-ion concentration of the reaction mixture was calculated using the relationship: $-\log [H^+] = pH - 0.10$. In this calculation, the activity coefficient of the hydrogen ions was estimated to 0.8 at $\mu=0.5$ from the data obtained by Kielland ($f_{H^+}=0.83$ at $\mu=0.2$).[12]

Results

The observed rate constant, k_{obsd}, defined by:

$$-d[Co(III)]/dt = k_{obsd}[Co(III)][Fe(II)] \quad (1)$$

was obtained from the slope of log $(A_t - A_\infty)$ *vs.* the time plot (A_t is the absorbance at time t, and A_∞, that at the time the reaction was completed). The plots were linear for at least for 2 half-lives in all cases The initial reactant concentrations were generally varied over at least a two-fold range, and a first-order dependence on the reactants was confirmed for the Co(III) and Fe(II).

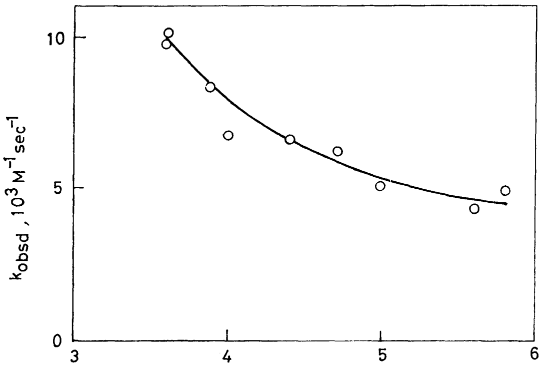

Fig. 1. Rate profile for the reduction of $Co(NH_3)_5Cl^{2+}$ by $Fe^{II}EDTA$.
$[Co(NH_3)_5Cl^{2+}] = 8-10 \times 10^{-4} M$, $[Fe^{II}EDTA] = 1.0 \times 10^{-2} M$, $\mu=0.50$, 25 °C.

Reduction of $Co(NH_3)_5Cl^{2+}$ by $Fe^{II}EDTA$. The values of k_{obsd} for the $Fe^{II}EDTA$ reduction of RCl^{2+} depend on the hydrogen-ion concentration. The rate profile for the reaction is shown in Fig. 1. The variation in the k_{obsd} with the pH indicates the following competition reactions:

$$Co(NH_3)_5Cl^{2+} + FeEDTA^{2-} \xrightarrow{k_n} Co(II) + Fe(III) \quad (2)$$

$$Co(NH_3)_5Cl^{2+} + FeHEDTA^{-} \xrightarrow{k_p} Co(II) + Fe(III) \quad (3)$$

The $FeHEDTA^-$ is the protonated species of Fe^{II}-EDTA, and k_n and k_p are the rate constants for the (2) and (3) reactions respectively. The amounts of free ferrous ion can be neglected under the present experimental conditions. The concentration of Fe(II) can be expressed by:

$$[Fe(II)] = [FeEDTA^{2-}] + [FeHEDTA^{-}] \quad (4)$$

The rate equation derived from Eqs. (2) and (3) is:

$$\text{Rate} = \frac{k_n + k_p K_{FeHY}[H^+]}{1 + K_{FeHY}[H^+]}[Co(III)][Fe(II)] \quad (5)$$

where K_{FeHY} is the formation constant for the protonated ferrous chelate. From a comparison of Eqs. (1) and (5), we obtain:

$$k_{obsd}(1 + K_{FeHY}[H^+]) = k_n + k_p K_{FeHY}[H^+] \quad (6)$$

The plots of $k_{obsd}(1 + K_{FeHY}[H^+])$ *vs.* $[H^+]$ form straight lines, and the slope and intercept of the line give the values of k_p and k_n respectively if the redox reaction can be expressed by the (2) and (3) reactions. The relationship between $k_{obsd}(1 + K_{FeHY}[H^+])$ *vs.* $[H^+]$ for the $Fe^{II}EDTA$ reduction is shown in Fig. 2. The value of K_{FeHY} used was $10^{2.8}$ [13]; this value was obtained under conditions of $\mu=0.1$ and 25 °C, and was used without any correction. The values of k_n and k_p, as calculated from the intercept and slopes of the straight line in Fig. 2, are $4.7 \times 10^3 M^{-1} sec^{-1}$ and $3.5 \times 10^4 M^{-1} sec^{-1}$ respectively at 25 °C and $\mu=0.50$.

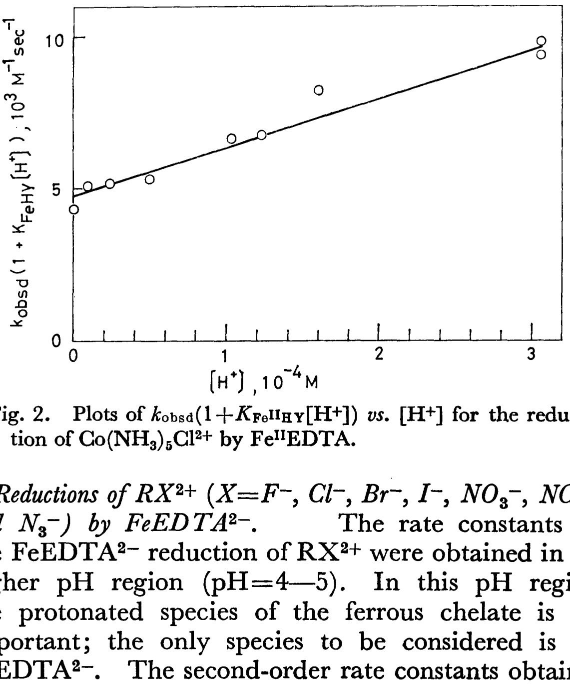

Fig. 2. Plots of $k_{obsd}(1 + K_{Fe^{II}HY}[H^+])$ *vs.* $[H^+]$ for the reduction of $Co(NH_3)_5Cl^{2+}$ by $Fe^{II}EDTA$.

Reductions of RX^{2+} ($X = F^-, Cl^-, Br^-, I^-, NO_3^-, NCS^-$, and N_3^-) by $FeEDTA^{2-}$. The rate constants for the $FeEDTA^{2-}$ reduction of RX^{2+} were obtained in the higher pH region (pH=4—5). In this pH region, the protonated species of the ferrous chelate is less important; the only species to be considered is the $FeEDTA^{2-}$. The second-order rate constants obtained are shown in Table 2.

TABLE 2. RATE CONSTANTS FOR THE $FeEDTA^{2-}$ REDUCTION OF PENTAAMMINECOBALT(III) COMPLEXES AT 25 °C AND $\mu=0.50$

Complex ($R = Co(NH_3)_5$)	k, $M^{-1}sec^{-1}$
RF^{2+}	6.0×10^3
RCl^{2+}	4.7×10^3 (3.5×10^4)[a]
RBr^{2+}	3.8×10^3
RI^{2+}	3.4×10^3
RNO^{3+}	~50
$RNCS^{2+}$	0.13
RN_3^{2+}	7.3×10^3

a) Rate constant for the $FeHEDTA^-$ reduction.

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[12] J. Kielland, *J. Amer. Chem. Soc.*, **59**, 1675 (1937).

[13] A. Ringbom, "Complexation in Analytical Chemistry," John Wiley and Sons, New York, 1963.

Reduction of $Co(NH_3)_5Cl^{2+}$ by $Fe^{II}Z^{m-}$ (Z=CyDTA, EDTA-OH, and DTPA). In the Fe^{II}CyDTA–RCl^{2+} and Fe^{II}EDTA-OH–RCl^{2+} reactions, the only predominant species of the ferrous chelate are the normal ones, $FeCyDTA^{2-}$ and $FeEDTA\text{-}OH^{-}$ respectively, under the experimental conditions employed. Therefore the second-order rate constants for these two reactions can simply be obtained from the rates evaluated in the pH region between 4 and 5. The rate constants thus obtained are shown in Table 3.

Table 3. Rate constants for the $FeCyDTA^{2-}$ and $FeEDTAOH^{-}$ reductions of $Co(NH_3)_5Cl^{2+}$ at 25 °C and $\mu=0.50$

Reductant	pH	k, $10^3 M^{-1} sec^{-1}$	Average value ($M^{-1} sec^{-1}$)
$FeCyDTA^{2-}$	4.0	2.6	
	4.4	2.9	
	5.0	2.9	2.9×10^3
$FeEDTAOH^{-}$	4.0	4.4	
	4.5	4.5	
	5.0	4.4	4.4×10^3

The rate constants for the $FeHDTPA^{2-}$–RCl^{2+} and $FeDTPA^{2-}$–RCl^{2+} reactions were obtained in the manner employed in the case of the Fe^{II}EDTA–RCl^{2+} reaction. The value of $K_{Fe^{II}HL}$ used for the calculation was $10^{5.4}$ (μ=0.1 and 25 °C).[13] The second-order rate constants were 4.8×10^3 $M^{-1} sec^{-1}$ for $FeHDTPA^{2-}$ and $\sim10^2$ $M^{-1} sec^{-1}$ for $FeDTPA^{3-}$. The rate constant for the $FeDTPA^{3-}$ may be less accurate, since the intercept of the straight line of the $k_{obsd}(1+K_{MHL}[H^+])$ *vs.* $[H^+]$ plot is relatively small.

Discussion

The relative rates for the reductions of Co(III)-pentaammine complexes by several reductants are shown in Table 4. It may be possible to assume that the reductions of RX^{2+} by Cr^{2+}[18] and, perhaps, by Fe^{2+} proceed *via* the inner-sphere mechanism, and those by $Cr(bipy)_3^{2+}$[4] and $Ru(NH_3)_6^{2+}$,[19] *via* the outer-sphere mechanism. If we accept the suggestion that Cr^{2+} reacts by means of a bridging mechanism,[19] is possible to suggest that the ligand, X, acts as the bridge in the Fe^{II}EDTA reductions of RX^{2+}. Furthermore, the large value of $k_{N_3^-}/k_{NCS^-}$ (=5.5×10^5), which can often be used to distinguish between an inner-sphere and an outer-sphere mechanism,[20] also indicates the inner-sphere nature of the reactions in the present system. Since the $Fe^{II}Z^{m-}$ complex ion is labile for the ligand exchange, one of the coordinated positions of the chelate could easily be open, so a bridged intermediate of the $[R\cdot X\cdot FeZ]^{(n-m)+}$ form might be formed prior to electron-transfer.

In the cases of X=F^-, Cl^-, Br^-, and I^-, the variation in the rate constants for FeY^{2-} (Y=$EDTA^{4-}$) shows the same tendency as Fe^{2+}; that is, the reactivity of the FeY^{2-} toward the RX^{2+} shows an "inverted order" of bridging efficiency:[18] $RF^{2+}>RCl^{2+}>RBr^{2+}>RI^{2+}$.

The relative rates for the reduction of RCl^{2+} by several ferrous chelate species are presented in Table 5. The results show that the decreasing order of the reactivities of the ferrous chelates is: $FeHEDTA^{-}>FeHDTPA^{2-}=FeEDTA^{2-}>FeEDTA\text{-}OH^{-}>FeCyDTA^{2-}>FeDTPA^{3-}$. This order shows that the rate does not depend so much on the charge of the chelate. The decreasing order of the values of "relative stabiliza-

Table 4. Relative rates[a] for the reductions of acidopentaamminecobalt (III) complexes at 25 °C and μ=1.0 (R=$Co(NH_3)_5$)

Complex	Reductant					
	$FeEDTA^{2-}$[b]	$FePDTA^{2-}$[c]	Fe^{2+}	Cr^{2+}	$Ru(NH_3)_6^{2+}$	$Cr(bipy)_3^{2+}$[j]
RF^{2+}	1.3	—	4.8[d]	0.4[g]	—	2×10^{-3}
RCl^{2+}	1.0	1.0	1.0[d]	1.0[g]	1.0[h]	1
RBr^{2+}	0.81	0.82	0.58[d]	2.3[g]	6.2[h]	6
RI^{2+}	0.72	—	—	5.0[g]	26[h]	—
RNO_3^{2+}	~0.01	—	—	6.4×10^{-4}[h]	—	—
$RNCS^{2+}$	2.7×10^{-5}	1.2×10^{-4}	1.8×10^{-3}[e]	1.4×10^{-5}[h]	—	1.3×10^{-2}
RN_3^{2+}	1.6	3.2	5.4[f]	0.5[h]	4.6×10^{-3}[i]	5×10^{-2}

a) Ratio of rate constant of RX^{2+} to that of RCl^{2+},
b) This work (μ=0.50),
c) From ref. 3,
d) From ref. 14 (μ=1.7),
e) From ref. 15,
f) From ref. 16,
g) From ref. 17,
h) From ref. 4,
i) From ref. 17 (μ=0.22),
j) From ref. 4 (μ=0.18).

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15) J. H. Espenson, *ibid.*, **4**, 121 (1965).

16) A. Haim, *J. Amer. Chem. Soc.*, **86**, 2352 (1964).

17) J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1966).

18) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

19) J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1686 (1964).

20) F. Basolo and R. G. Pearson "Mechanism of Inorganic Reaction," 2nd Ed., John Wiley and Sons, New York (1958), p. 482.

TABLE 5. COMPARISON OF REACTIVITY FOR FeZ^{m-}-REDUCTIONS OF Co(NH$_3$)$_5$Cl^{2+} AT 25 °C AND μ=0.50

Complex	Relative rate
FeEDTA^{2-}	1.0
FeCyDTA^{2-}	0.62
FeEDTA-OH$^-$	0.94
FeDTPA^{3-}	0.02
FeHEDTA$^-$	6.0
FeHDTPA^{2-}	1.0

TABLE 6. VALUES OF log $K_{\mathrm{Fe^{III}Z}}/K_{\mathrm{Fe^{II}Z}}$ OF Fe(III)-Fe(II) REDOX COUPLES

Redox couple	log $K_{\mathrm{Fe^{III}Z}}/K_{\mathrm{Fe^{II}Z}}$ (R_s)$^{a)}$
FeEDTA$^-$/FeEDTA^{2-}	0.25
FeEDTA-OH/FeEDTA-OH$^-$	0.21
FeCyDTA$^-$/FeCyDTA^{2-}	0.21
FeDTPA^{2-}/FeDTPA^{3-}	0.24
FeEDT$^-$/FeHEDTA$^-$ $^{b)}$	0.95
FeDTPA^{2-}/FeHDTPA^{2-} $^{b)}$	0.71

a) The values are calculated using formation constants estimated at 25 °C and μ=0.1.[13)]

tion," which is expressed by R_s, in Table 6 is: FeHEDTA$^-$ > FeHDTPA^{2-} > FeEDTA^{2-} FeDTPA^{3-}> FeEDTA-OH$^-$=FeCyDTA^{2-}. For the FeHEDTA$^-$ and FeHDTPA^{2-} reductions, the predominant species of the oxidized forms which are formed in the solutions are normal ferric chelates, Fe^{III}EDTA$^-$, and Fe^{III}DTPA^{2-} respectively under the experimental conditions employed. Therefore, the values of R_s for FeHEDTA$^-$ and FeHDTPA^{2-} are evaluated on the basis of the change from a protonated ferrous chealte to a normal ferric chelate. The decreasing order of reactivity agrees with that of R_s except for FeDTPA^{3-}. Such a correspondence between the order of reactivity and that of R_s suggests that one of the most important factors controlling the rates of the ferrous chelate reductions of RX^{2+} is the effect of the relative stabilization (stabilization effect). This indicates that there is some correlation between ΔF and $\Delta F^{\ast}$ for the reaction. The smaller reactivity for FeDTPA^{3-} may be due to the steric hindrance of the bulky ligand.

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