Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Oxidation of Aminopolycarboxylate Complexes of Bivalent Transition Metals by Halogens. Mechanism and Free Energy Relationships

WILLIAM H. WOODRUFF and DALE W. MARGERUM*

Received November 29, 1973

AIC308675

The mechanisms of oxidation of $M^{II}L^{2-}$ to the M^{III} complexes by X_2 and X_3^- are studied where M is iron, cobalt, and manganese, X is iodine and bromine, and L is EDTA and *trans*-1,2-diaminocyclohexanetetraacetate (CyDTA). The reactions are first order in $M^{II}L^{2-}$ concentration and first order in total halogen concentration. The rate constants for the iron(II) reactions are 9–11 orders of magnitude greater than those for the analogous manganese(II) and cobalt(II) reactions. A general mechanism for these reactions is proposed in which a one-electron reduction of the halogens takes place after inner-sphere coordination. However, the activation parameters and the rate constants indicate that the position of the rate-determining step differs with the reactant pairs examined. The rates of oxidation of $Fe^{II}L^{2-}$ by Br_2, Br_3^-, and I_2 appear to be controlled by the rate at which the oxidant enters the coordination sphere of the metal ion. The rates of oxidation of $Fe^{II}L^{2-}$ by I_3^- and of $Co^{II}L^{2-}$ and $Mn^{II}L^{2-}$ by X_2 and X_3^- are limited by the electron-transfer process subsequent to the coordination of the oxidant. Marcus-type free energy correlations are found for the latter inner-sphere reactions plus the reactions of V^{2+}(aq) and Fe^{2+}(aq) with halogens, spanning large ranges in the $\Delta G°$ value for the one-electron redox reactions. This permits self-exchange electron-transfer rate constants to be estimated as $8.5 \times 10^4\ M^{-1}\ sec^{-1}$ for I_2, I_2^- and $29\ M^{-1}\ sec^{-1}$ for Br_2, Br_2^-.

Introduction

Previous papers in this series concerned the oxidation of $Fe^{II}CyDTA^{2-}$ by iodine[1] and the oxidations of $Co^{II}L^{2-}$ (L = EDTA, CyDTA) by bromine and iodine.[2] We now report the kinetics of the oxidation of $Fe^{II}EDTA^{2-}$ by iodine, of $Fe^{II}CyDTA^{2-}$ by bromine, and of $Mn^{II}EDTA^{2-}$ by bromine. The thermochemical parameters of the $Fe^{II}CyDTA^{2-}$, $Fe^{III}CyDTA^-$ redox couple are also reported. With these data a general mechanism may be proposed for the reaction in eq 1,

$$2M^{II}L^{2-} + \left[\begin{array}{c} X_2 + X^- \\ \uparrow\downarrow \\ X_3^- \end{array}\right] \rightarrow 2M^{III}L^- + 3X^- \qquad (1)$$

where M is a transition metal (iron, cobalt, or manganese), L is an EDTA-like ligand, and X is a halogen. This mechanism fits the experimental observations made for reaction 1, despite the huge reactivity differences among the various reactant pairs.

Although the reactions studied (eq 1) follow an inner-sphere mechanism and the oxidant is not a metal center, the reactions conform to Marcus theory[3,4] free energy relationships. Halogen oxidations of other metal centers (Fe^{2+}(aq) and V^{2+}(aq)) studied by previous workers[5,6] also fit this behavior. Therefore the reactivity differences in the metal complex–halogen reactions can be explained in terms of Marcus theory. Values are calculated for the self-exchange rate constants of iodine and bromine. These values cannot be measured directly due to the extremely rapid atom-transfer reactions of these species.

Experimental Section

Reagents and Materials. The sodium salt of $Mn^{II}(EDTA)^{2-}$ was prepared in the same manner as described for the corresponding cobalt(II) salts.[2] The elemental analysis corresponded to $Na_2Mn^{II}(EDTA)\cdot 0.5H_2O$. General procedures were the same as previously reported.[1,2]

Instrumentation. Fast reactions (*i.e.*, those of $Fe^{II}L^{2-}$) were followed using a Durrum stopped-flow spectrophotometer interfaced to a Hewlett-Packard 2115A general-purpose computer (8K × 16 bit memory) as described elsewhere.[7] Using this system, data are acquired on-line and transferred into core memory at a maximum rate of 100 μsec/point. An oscilloscope display of the appropriate rate law plot can be obtained within 1 min of the completion of a kinetics experiment, along with a least-squares rate constant for that experiment.

Slower reactions were followed in the same manner employed for the oxidations of $Co^{II}L^{2-}$.[2] Measurements of pH were made using an Instrumentation Laboratory 245 pH meter with a calomel reference electrode containing saturated NaCl. Other potentiometric measurements were made using a Radiometer PHM-26 meter, a bright platinum indicating electrode, and a saturated calomel reference electrode. Temperature control was maintained within ±0.1° for all studies.

Species concentration calculations were performed using a modified version of the program COMICS.[8] Error limits quoted for the observed stopped-flow rate constants refer to the standard deviation of four to ten experiments. Error limits for resolved rate constants and activation parameters refer to the standard deviations of the slope and intercept of the appropriate linear least-squares fit.

Results

General Data. All of the reactions studied were first order in total halogen concentration and first order in metal chelate concentration. The rate constants due to the reactions of molecular halogen and of trihalide ion were resolved in the manner previously reported.[1,2] The second-order rate constant is designated k_0 throughout this work and is defined such that $-d([X_2]_T)/dt = k_0[X_2]_T[M^{II}L^{2-}]$, where $[X_2]_T = [X_2] + [X_3^-]$. The notation used to identify the rate constants due to X_2 and X_3^- is

$$M^{II}L^{2-} + X_2 \xrightarrow{k_1} \text{products} \qquad (2)$$

and

$$M^{II}L^{2-} + X_3^- \xrightarrow{k_2} \text{products} \qquad (3)$$

with the reaction designated by k_n having activation parameters $\Delta H_n^\ddagger$ and $\Delta S_n^\ddagger$.

The $Fe^{II}(EDTA)^{2-}$–Iodine Reaction. The conditions under which this reaction was studied were identical with those used previously[1] for the $Fe^{II}(CyDTA)^{2-}$–iodine system, ex-

---

(1) W. H. Woodruff, D. C. Weatherburn, and D. W. Margerum, *Inorg. Chem.*, 10, 2102 (1971).

(2) W. H. Woodruff, B. A. Burke, and D. W. Margerum, *Inorg. Chem.*, 13, 2573 (1974).

(3) R. A. Marcus, *Annu. Rev. Phys. Chem.*, 15, 115 (1964).

(4) R. A. Marcus, *J. Phys. Chem.*, 72, 891 (1968).

(5) J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, 8, 1407 (1969).

(6) P. R. Carter and N. Davidson, *J. Phys. Chem.*, 56, 877 (1952).

(7) B. G. Willis, J. A. Bittikoffer, H. L. Pardue, and D. W. Margerum, *Anal. Chem.*, 42, 1340 (1970).

(8) D. D. Perrin and I. G. Sayce, *Talanta*, 14, 833 (1967).

Table I. Kinetics Data for the Oxidation of $Fe^{II}(EDTA)^{2-}$ by Iodine[a]

$[I^-]$, M	Temp, °C	$10^{-4}k_0$, M^{-1} sec^{-1}
0.025	10.0	3.0 ± 0.2
0.05	10.0	1.57 ± 0.05
0.10	10.0	0.84 ± 0.03
0.15	10.0	0.56 ± 0.02
0.025	25.0	8.0 ± 0.1
0.05	25.0	4.6 ± 0.5
0.10	25.0	2.59 ± 0.06
0.15	25.0	1.77 ± 0.05
0.05	40.2	13 ± 1
0.075	40.2	9.2 ± 0.7
0.125	40.2	5.5 ± 0.3
0.15	40.2	4.9 ± 0.3

[a] $[Fe^{II}(EDTA)^{2-}]_0 = 5.00 \times 10^{-4}\ M$; $([I_2]_T)_0 = 2.50 \times 10^{-4}\ M$; $\mu = 0.2$ (NaClO$_4$ + NaI); pH 4.8-5.2; $[EDTA]_T = 10^{-2}\ M$.

Table II. Resolved Rate Constants for the Reactions of I_2 and I_3^- with $Fe^{II}(EDTA)^{2-}$

Temp, °C	$K_{I_3^-}$, M^{-1}	k_1, M^{-1} sec^{-1}	k_2, M^{-1} sec^{-1}
10.0	1215	$(9.4 \pm 0.2) \times 10^5$	$(5.0 \pm 1.6) \times 10^2$
25.0	768	$(1.60 \pm 0.08) \times 10^6$	$(4.4 \pm 1.1) \times 10^3$
40.2	503	$(3.2 \pm 0.2) \times 10^6$	$(7.4 \pm 3.1) \times 10^3$

cept that the present study was carried out at pH 5 to ensure complete formation of $Fe^{II}(EDTA)^{2-}$. Table I presents the observed kinetic data for the oxidation of $Fe^{II}(EDTA)^{2-}$ by iodine. The resolved values of k_1 and k_2 at each temperature studied are given in Table II, and the graphical resolution is shown in Figure 1. The values used for the stability constant of I_3^- at the various temperatures are given in Table II.[1]

The $Fe^{II}(CyDTA)^{2-}$-Bromine Reaction. Special procedures were required in carrying out this study, due to the air sensitivity of $Fe^{II}L^{2-}$ and to the fact that bromine reacts fairly rapidly with uncoordinated aminocarboxylates. (The reaction between L and bromine does not proceed at an appreciable rate when L is coordinated to Mn^{2+}, Co^{2+}, Ni^{2+}, or Cu^{2+}.) This necessitated the preparation of a solution of $Fe^{II}(CyDTA)^{2-}$, rather than forming the chelate *in situ* as was possible in the iodine oxidations. The $Fe^{II}(CyDTA)^{2-}$ solution must be kept free of oxygen until it is mixed with the bromine solution in the stopped-flow apparatus.

Solutions containing $4.0 \times 10^{-4}\ M$ $Fe^{II}(CyDTA)^{2-}$ were prepared by deaerating 98 ml of a solution containing 0.02 M CyDTA and appropriate concentrations of sodium perchlorate and sodium bromide. The deaerating gas was 99.99% helium. Iron(II) was then introduced by adding 2 ml of 0.0200 M $Fe(NH_4)_2(SO_4)_2$ solution. The resulting solution was transferred to the stopped-flow instrument using syringe techniques.[9] The bromine solutions ($2.0 \times 10^{-4}\ M$) were not deaerated, since the air oxidation of $Fe^{II}(CyDTA)^{2-}$ is slow[10] compared to the very fast bromine oxidation. In addition to sodium perchlorate and sodium bromide, the bromine solutions contained 0.1 M acetate buffer, pH 3.7. The reactions were followed at 360 nm, where the initial bromine absorbance gives way to the stronger absorbance of $Fe^{III}(CyDTA)^-$. The speed of the oxidation of $Fe^{II}(CyDTA)^{2-}$ by bromine is such that, under the conditions described, all of the reactions were complete in 35-100 msec.

The data for the $Fe^{II}(CyDTA)^{2-}$-bromine reaction are summarized in Table III. The graphical resolution of k_1 and k_2 is shown in Figure 2. The higher ionic strength ($\mu = 1.1$ compared to $\mu = 0.2$ in the $Fe^{II}L^{2-}$-iodine reactions) was necessary due to the lower stability of Br_3^- (compared to I_3^-) and the concomitant necessity to employ high bromide ion concentrations. The value used for the stability constant of Br_3^- at 25.0° was 16.85 M^{-1}.[11]

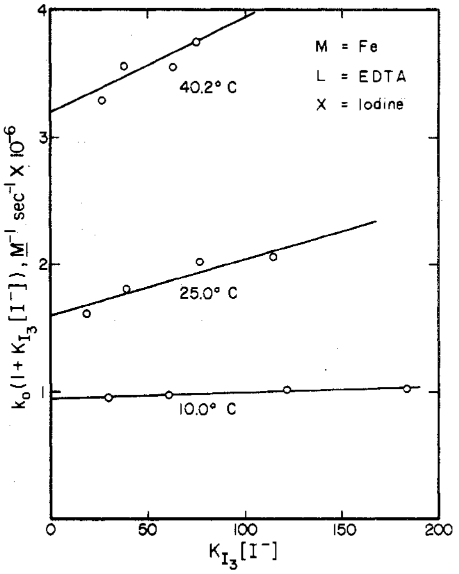


Figure 1. Plot of data used to resolve k_1 (intercept) and k_2 (slope) for the oxidation of $Fe^{II}EDTA^{2-}$ by $(I_2)_T$ at the temperatures studied.

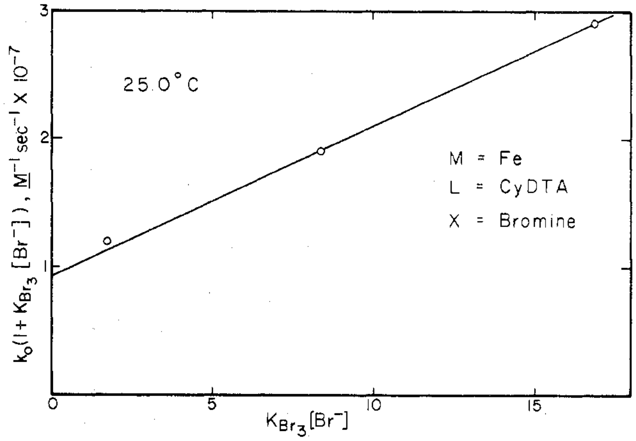


Figure 2. Plot of data used to resolve k_1 (intercept) and k_2 (slope) for the oxidation of $Fe^{II}CyDTA^{2-}$ by $(Br_2)_T$ at 25.0°.

Table III. Kinetics Data for the Oxidation of $Fe^{II}(CyDTA)^{2-}$ by Bromine at 25.0°[a]

$[Br^-]_T$, M	$10^{-6}k_0$, M^{-1} sec^{-1}
0.10	4.3 ± 0.4
0.50	2.0 ± 0.2
1.00	1.6 ± 0.1

$k_1 = (9.3 \pm 0.6) \times 10^6\ M^{-1}$ sec^{-1}
$k_2 = (1.16 \pm 0.05) \times 10^6\ M^{-1}$ sec^{-1}

[a] $[Fe^{II}(CyDTA)^{2-}]_0 = 2.00 \times 10^{-4}\ M$; $([Br_2]_T)_0 = 0.91 \times 10^{-4}\ M$; acetate buffer, pH 3.7; $\mu = 1.1$ (NaClO$_4$ + NaBr); $[CyDTA]_T = 0.01$ M.

The $Mn^{II}(EDTA)^{2-}$-Bromine Reactions. This study was performed in a similar manner to that of the $Co^{II}L^{2-}$-bromine reactions.[2] An interference is present in the $Mn^{II}(EDTA)^{2-}$-bromine reactions which was not present in the cobalt systems, in that $Mn^{II}(EDTA)^{2-}$ dissociates significantly to Mn^{2+}(aq) and free EDTA. The free ligand then reacts with bro-

---

(9) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, p 154.

(10) Y. Kurimura, R. Ochiai, and N. Matsuura, *Bull. Chem. Soc. Jap.*, 41, 2234 (1968).

(11) D. B. Scaife and H. J. V. Tyrell, *J. Chem. Soc.*, 386 (1958); J. M. Pink, *Can. J. Chem.*, 48, 1169 (1970).

mine as noted earlier. Bromide ion inhibits the reaction between L and $(Br_2)_T$ to a greater degree than it inhibits the oxidation to $Mn^{III}L^-$. For this study the dissociation of $Mn^{II}(EDTA)^{2-}$ was suppressed by carrying out the oxidations in the presence of excess Mn^{2+}(aq). However, recent work by Vierling and Margerum[12] shows that increased concentrations of Mn^{2+}(aq) in the presence of bromine will catalyze the formation of $Mn^{III}L^-$. This reaction product is not stable and decomposes at a rate comparable to its rate of formation. The data in Table IV were obtained by initial rate methods and by extrapolation of the rate constants to zero Mn^{2+} concentration.[12] The graphical resolution of the k_1 and k_2 rate constants for Br_2 and Br_3^-, respectively, is shown in Figure 3. The reactions were monitored at 510 nm, the absorption maximum for $Mn^{III}(EDTA)^-$,[13,14] and at 560 nm where there is less interference from the Br_2 absorbance. The $[Br^-]$ in the second column of Table IV is the free bromide ion concentration after correction for Br_3^- formation.

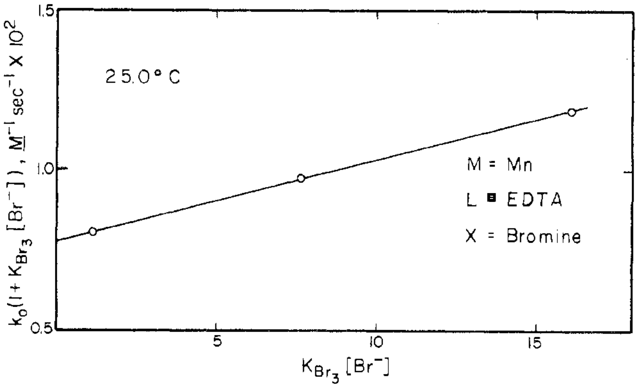


Figure 3. Plot of data used to resolve k_1 (intercept) and k_2 (slope) for the oxidation of $Mn^{II}EDTA^{2-}$ by $(Br_2)_T$ at 25.0°.

Table IV. Kinetics Data for the Oxidation of $Mn^{II}(EDTA)^{2-}$ by Bromine at 25.0°[a]

$[Br^-]_T$, M	$[Br^-]$, M	10^3k_0, M^{-1} sec^{-1}
0.100	0.073	3.7
0.500	0.456	1.1
1.000	0.953	0.7

$k_1 = (7.8 \pm 0.2) \times 10^{-3} M^{-1}$ sec^{-1}
$k_2 = (2.5 \pm 0.2) \times 10^{-4} M^{-1}$ sec^{-1}

[a] $[Mn^{II}(EDTA)^{2-}]_0 = 1.00 \times 10^{-3}$ M; $[Br_2]_T = 5.0 \times 10^{-2}$ M; 0.1 M acetate buffer, pH 3.7; $\mu = 1.1$ ($NaClO_4$ + NaBr); $[Mn^{2+}(aq)] =$ 0.005-0.02 M (range used for extrapolation); $K_{Br_3} = 16.85$ M^{-1}.

Table V. Potential of the $Fe^{II}(CyDTA)^{2-}$, $Fe^{III}(CyDTA)^-$ Couple *vs.* Sce as a Function of Temperature[a]

Temp, °K	E_{cell}, mV	ΔG_{cell}, kcal mol^{-1}
286.1	143	−6.60
290.4	146	−6.73
297.2	149	−6.87
304.6	153	−7.06
308.4	156	−7.20

$\Delta H_{cell} = +0.8 \pm 0.4$ kcal mol^{-1}
$\Delta S_{cell} = +26 \pm 1$ eu

[a] $[Fe^{II}(CyDTA)^{2-}] = [Fe^{III}(CyDTA)^-] = 2 \times 10^{-3}$ M; $\mu = 0.1$ ($NaClO_4$); $[CyDTA]_T = 8 \times 10^{-3}$ M; pH 4.0 (acetate buffer).

The $Fe^{II}(CyDTA)^{2-}$, $Fe^{III}(CyDTA)^-$ Redox Couple.

Knowledge of the ΔH° and ΔS° values for eq 4 is desirable

$$Fe^{II}(CyDTA)^{2-}(aq) + H^+(aq) = Fe^{III}(CyDTA)^-(aq) + {}^1/_2H_2(g) \qquad (4)$$

in the interpretation of the mechanism of the oxidation of $Fe^{II}L^{2-}$. The free energy change of reaction 4 has been measured potentiometrically (as E°) by previous workers.[15,16] In the present study similar measurements were made as a function of temperature, in order to determine ΔH° and ΔS°. The concentrations of iron(II) and iron(III) were equal (2×10^{-3} M). The pH and ionic strength were essentially the same as those under which the $Fe^{II}L^{2-}$ plus iodine kinetic studies were performed. The general procedure for the potentiometric measurements has been described by others.[17,18] Air was excluded from the cell in which these measurements were made. The effect of liquid junction potential was considered to be constant and negligible.[18] The results are summarized in Table V. Using the value[19] for the temperature coefficient of the saturated calomel electrode, thermochemical parameters for reaction 4 of $\Delta H^\circ = +11.2 \pm 0.4$ kcal mol^{-1} and $\Delta S^\circ = +31 \pm 1$ eu are calculated.

It is now possible to calculate ΔH° and ΔS° for reaction 5

$$Fe^{3+}(aq) + CyDTA^{4-}(aq) = Fe^{III}(CyDTA)^-(aq) \qquad (5)$$

using published ΔH° and ΔS° values for the reactions in eq 6[20] and in eq 7[16,21] in a Born-Haber cycle. The thermochemical parameters calculated for reaction 5 (which have not been previously reported) are $\Delta H^\circ = -6.0$ kcal mol^{-1} and $\Delta S^\circ = +116$ eu. From these ΔH° and ΔS° values, an equilibrium constant for reaction 5 is calculated as $\log K = 29.77$. This compares with the published value[15] of $\log K = 29.27$. A similar large positive ΔS° value (+117 eu) has been found for the complexation of Al^{3+} by $EDTA^{4-}$.[22]

$$Fe^{2+}(aq) + H^+(aq) = Fe^{3+}(aq) + {}^1/_2H_2(g) \qquad (6)$$

$$Fe^{2+}(aq) + CyDTA^{4-}(aq) = Fe^{II}(CyDTA)^{2-}(aq) \qquad (7)$$

Discussion

Table VI summarizes the rate constants at 25.0° and the activation parameters for the systems under study. A striking fact evident from this table is that the iron reactions are many orders of magnitude faster than the analogous cobalt reactions. Table VII presents the ΔG° values for the reactions studied, both for the overall reaction and for the initial step of a one-electron mechanism. Comparison of the data in Tables VI and VII shows that, while the oxidation of $Co^{II}(CyDTA)^{2-}$ by Br_2 is thermodynamically more favorable than the oxidation of $Fe^{II}(CyDTA)^{2-}$ by I_2, the latter reaction is 9 orders of magnitude faster than the former.

Four other general observations should be made concerning the data in Table VI. First, the ratio k_1/k_2 is 2-3 for most of the cobalt reactions; it is 8 for the $Fe^{II}(CyDTA)^{2-}$-

---

(12) F. Vierling and D. W. Margerum, to be submitted for publication.

(13) Y. Yoshino, A. Ouchi, T. Tsunoda, and M. Kojima, *Can. J. Chem.*, 40, 775 (1962).

(14) R. E. Hamm and M. A. Suwyn, *Inorg. Chem.*, 6, 139 (1967).

(15) J. Bond and T. J. Jones, *Trans. Faraday Soc.*, 55, 1310 (1959).

(16) M. M. T. Khan and A. E. Martell, *J. Amer. Chem. Soc.*, 90, 3386 (1968).

(17) H. Rosotti, "Chemical Applications of Potentiometry," Van Nostrand, London, 1969, Chapter 7.

(18) G. I. H. Hanania, D. H. Irvine, W. A. Eaton, and P. George, *J. Phys. Chem.*, 71, 2022 (1967).

(19) J. J. Lingane, "Electroanalytical Chemistry," Interscience, New York, N. Y., 1958.

(20) *Nat. Bur. Stand.* (*U. S.*), *Circ.*, No. 500 (1952).

(21) D. L. Wright, J. H. Holloway, and C. N. Reilley, *Anal. Chem.*, 37, 884 (1965).

(22) A. S. Carson, P. G. Laye, and P. N. Smith, *J. Chem. Soc. A*, 527 (1968).

Table VI. Kinetics Data for the Oxidation of $M^{II}L^{2-}$ by X_2 (k_1) and X_3^- (k_2) at 25.0°[a]

Reactants	k_1, M^{-1} sec^{-1}	$\Delta H_1^\ddagger$, kcal mol^{-1}	$\Delta S_1^\ddagger$, eu	k_2, M^{-1} sec^{-1}	$\Delta H_2^\ddagger$, kcal mol^{-1}	$\Delta S_2^\ddagger$, eu
$Fe^{II}(CyDTA)^{2-}$ [b] (I_2, I_3^-)	1.24×10^6	7.7 ± 0.3	−5 ± 1	5.0×10^3	21 ± 3	+28 ± 9
$Fe^{II}(EDTA)^{2-}$ [c] (I_2, I_3^-)	1.60×10^6	7.5 ± 0.3	−5 ± 1	4.4×10^3	17 ± 3	+15 ± 9
$Fe^{II}(CyDTA)^{2-}$ [c] (Br_2, Br_3^-)	9.3×10^6			1.16×10^6		
$Co^{II}(CyDTA)^{2-}$ [d] (I_2, I_3^-)	6.4×10^{-5}	21.0 ± 0.3	−7.3 ± 0.8	2.2×10^{-5}	21.1 ± 0.7	−9 ± 2
$Co^{II}(EDTA)^{2-}$ [d] (I_2, I_3^-)	5.2×10^{-4}	23 ± 2	+1 ± 6	3.1×10^{-5}	25 ± 3	+5 ± 9
$Co^{II}(CyDTA)^{2-}$ [d] (Br_2, Br_3^-)	2.0×10^{-3}	18.3 ± 0.3	−9.5 ± 0.9	1.11×10^{-3}	18.0 ± 0.3	−12 ± 1
$Co^{II}(EDTA)^{2-}$ [d] (Br_2, Br_3^-)	7.3×10^{-2}			5.42×10^{-2}		
$Mn^{II}(EDTA)^{2-}$ [e] (Br_2, Br_3^-)	7.8×10^{-3}			2.5×10^{-4}		

[a] Activation parameters for cobalt reactions were taken between 25 and 55° (bromine) or 71.5° (iodine). [b] Reference 1. [c] Present work. [d] Reference 2. [e] Reference 12.

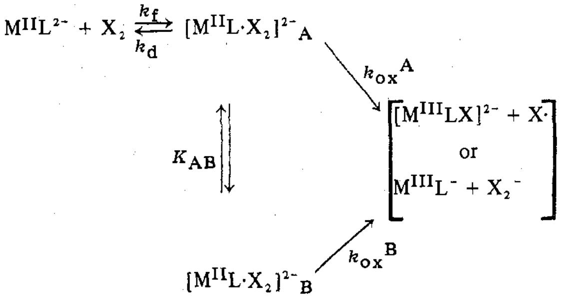
Table VII. Free Energy Changes[a,b] at 25.0° for Reactions under Study

	$\Delta G°$, kcal mol^{-1}			$\Delta G°$, kcal mol^{-1}	
Reactants	Overall[c]	One-electron[d]	Reactants	Overall[c]	One-electron[d]
$Fe^{II}L^{2-}$, Br_2	−46.1	−9.7	$Fe^{II}L^{2-}$, I_3^-	−21.2	+3.4
$Fe^{II}L^{2-}$, Br_3^-	−43.8	−8.0	$Co^{II}L^{2-}$, I_2	−11.5	+6.0
$Co^{II}L^{2-}$, Br_2	−32.7	−3.2	$Mn^{II}L^{2-}$, Br_2	−12.5	+7.2
$Co^{II}L^{2-}$, Br_3^-	−30.4	−1.5	$Mn^{II}L^{2-}$, Br_3^-	−10.2	+8.9
$Fe^{II}L^{2-}$, I_2	−24.9	−0.5	$Co^{II}L^{2-}$, I_3^-	−7.8	+9.9

[a] Calculated from data in following sources: iron, present work and ref 15; cobalt, F. L. Garvan in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, Chapter 7; manganese, N. Tanaka and H. Ogino, *Bull. Chem. Soc. Jap.*, 38, 1515 (1965); halogens (two-electron), W. L. Latimer, "Oxidation Potentials," Prentice-Hall, Englewood Cliffs, N. J., 1952, p 59; H. A. Laitinen, "Chemical Analysis," McGraw-Hill, New York, N. Y., 1960, p 393; halogens (one-electron), W. H. Woodruff and D. W. Margerum, *Inorg. Chem.*, 12, 962 (1973). [b] The tabulated values of $\Delta G°$ are for L = CyDTA. The $\Delta G°$ values for L = EDTA are approximately 0.75 kcal equiv^{-1} more positive in each case. [c] Equation 1. [d] $M^{II}L^{2-} + X_2 \rightarrow M^{III}L^- + X_2^-$ or $M^{II}L^{2-} + X_3^- \rightarrow M^{III}L^- + X_2^- + X^-$.

Chart I. General Mechanism for the Oxidation of $M^{II}L^{2-}$ by Halogens

I. Rate-determining process: rate of coordination (k_f step) or the one-electron reduction of X_2 (k_{ox} step).



II. Rapid post-electron-transfer process: halogen radical recombination

or

$M^{II}L^{2-} + (X\cdot)_T \rightarrow [M^{III}LX]^{2-}$

III. Elimination of the coordinated halide ion (slow or rapid)

$[M^{III}LX]^{2-} \rightarrow [M^{III}L]^- + X^-$

bromine reaction and 31 for the manganese reactions, but it is 250–400 for the $Fe^{II}L^{2-}$-iodine reactions. Second, the rate constants for the oxidation of $Fe^{II}L^{2-}$ by I_2, Br_2, and Br_3^- are all of the same order of magnitude (10^6 M^{-1} sec^{-1}) despite the large differences in $\Delta G°$ for these reactions (see Table VII). Third, comparing $\Delta S_1^\ddagger$ to $\Delta S_2^\ddagger$ in each horizontal row of Table VI, the values are seen to be similar within each cobalt reaction but quite different in the two iron reactions. Furthermore, the difference between $\Delta S_1^\ddagger$ and $\Delta S_2^\ddagger$ in the iron reactions is in the opposite direction of that predicted from the electrostatic repulsion in bringing together two ions of like charge.[23] Finally, comparing the rate constants for a given metal and oxidant between the EDTA and CyDTA complexes, the EDTA reactions are faster in every case for cobalt but not for iron. That is to say, there is little evidence for steric compression effects[2] in the iron reactions.

General Mechanism. Previous studies with the cobalt(II) oxidations[2] have shown that these are inner-sphere reactions. The kinetic evidence indicates that the other metal centers also react with the halogens in an inner-sphere mechanism.[1] Additional mechanistic interpretations are that the oxidations of $Fe^{II}L^{2-}$ by I_2, Br_2, and Br_3^- are controlled by the rate of coordination of the oxidant to the metal ion. On the other hand the oxidation of $Fe^{II}L^{2-}$ by I_3^-, as well as the cobalt and manganese reactions, is controlled by the electron-transfer process (with attendant reorganizations) subsequent to coordination of the oxidant. Finally, the transition state in the $Fe^{II}L^{2-}$-I_3^- reactions differs from that in the cobalt reactions, in that the former is more similar to products and less sterically constrained than the latter.

The proposed general mechanism for the oxidation of $M^{II}L^{2-}$ by halogens is given in Chart I. The mechanism is written for X_2 but is equally applicable to X_3^-. As indicated earlier, k_f is the rate-determining step for the oxidation of $Fe^{II}L^{2-}$ by Br_2, Br_3^-, and I_2. On the other hand, in the oxidation of $Fe^{II}L^{2-}$ by I_3^-, $k_{ox}{}^A$ is proposed as the rate-determining step, while in the oxidation of $Co^{II}L^{2-}$ by X_2 and X_3^-, $k_{ox}{}^B$ is proposed as the rate-determining step. Two intermediate species are proposed which contain X_2 in the inner coordination sphere of the metal ion. The notation $[M^{II}L\cdot X_2]^{2-}{}_A$ designates an intermediate having a coordination number greater than 6, while $[M^{II}L\cdot X_2]^{2-}{}_B$ denotes a six-coordinate intermediate.

Nature of the Intermediates. The proposal of two intermediate species results partially from the steric compression argument.[2] The ratios of k_n/k'_n (where k_n refers to $M^{II}(EDTA)^{2-}$ and k'_n refers to $M^{II}(CyDTA)^{2-}$) are 8.1, 1.4, 36, and 49 for the Co^{II} reactions. The larger ratios are charac-

---

(23) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 145.

teristic of the relative stabilities of mixed complexes with metal-EDTA *vs.* metal-CyDTA. However, the ratio of k/k' for the oxidation of $Fe^{II}L^{2-}$ by I_3^- does not show this characteristic ratio and is only 0.9. The steric compression effect manifests itself in the configurational equilibrium represented by K_{AB} in Chart I.

Another reason for proposing the "A" and "B" intermediates lies in the activation parameters of $Fe^{II}L^{2-}$-iodine reactions. The very large $\Delta H_2^{\ddagger}$ values (relative to $\Delta H_1^{\ddagger}$) suggest that the more difficult electron transfer to I_3^- is not compensated by the increased Lewis basicity of I_3^- as it is for the $Co^{II}L^{2-}$ reactions. The large positive $\Delta S_2^{\ddagger}$ values for the $Fe^{II}L^{2-}$-I_3^- reactions relative to the $Co^{II}L^{2-}$-I_3^- reactions indicate different configurations of the activated complexes for the two metals.

Structures of EDTA and CyDTA complexes have been determined in which the ligands are pentadentate and the complexes are six-coordinate.[24,25] In other cases these ligands are hexadentate and the complexes are seven-coordinate.[26,27] Both of these structures are believed to exist in solution.[28-32] Some of the complexes, especially those of iron(III), may exist in either configuration depending upon conditions.[24,27,31,32] Therefore the structures of $[M^{II}L\cdot X_2]^{2-}{}_A$ and $[M^{II}L\cdot X_2]^{2-}{}_B$ may be as shown (for L = CyDTA) in Figure 4, where the "A" species is seven-coordinate and where X_2 has displaced a carboxylate group of L in $[M^{II}L\cdot X_2]^{2-}{}_B$.

The fact that the k_1/k_2 ratios for the $Co^{II}L^{2-}$ reactions are small can be explained by the stronger Lewis basicity of X_3^- compared to X_2.[2] The six-coordinate "B" intermediate should be a better electron-pair acceptor than the "A" intermediate with its expanded coordination geometry. Thus, K_{AB} will be larger for X_3^- than it is for X_2. The second-order rate constant for reactions proceeding by the "B" intermediate will be $(k_f/k_d)K_{AB}k_{ox}{}^B$ and the more favorable K_{AB} values for X_3^- apparently offset the electrostatic effects on k_f/k_d and $k_{ox}{}^B$. On the other hand the k_1/k_2 ratios are large for the $Fe^{II}L^{2-}$-iodine reactions (the ratios are 248 and 364 for the CyDTA and EDTA complexes), which are believed to have electron transfer *via* the "A" intermediate. Indeed the I_2 path is so much favored over the I_3^- path for $Fe^{II}L^{2-}$ that the I_2 reaction appears to be limited by its rate of inner-sphere coordination. The second-order rate constant for the "A" pathway is $k_fk_{ox}{}^A/(k_d + k_{ox}{}^A)$, but for the reactions of I_2, Br_2, and Br_3^- with $Fe^{II}L^{2-}$ it is proposed that $k_{ox}{}^A >> k_d$ so that the observed rate constant equals k_f. The k_1/k_2 ratio is only 8 for Br_2 and Br_3^- with $Fe^{II}CyDTA^{2-}$ as both reactions approach the substitution-controlled rate. On the other hand it is suggested that $k_{ox}{}^A << k_d$ for the I_3^- reaction with $Fe^{II}L^{2-}$ so that the observed rate constant is $(k_f/k_d)k_{ox}{}^A$.

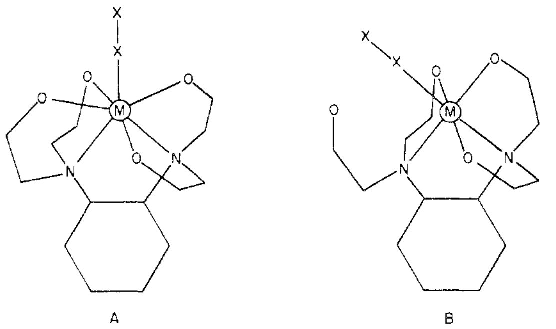


Figure 4. Possible structures of the intermediates in the proposed general mechanism (Chart I): A, $([M^{II}L\cdot X_2]^{2-})_A$; B, $([M^{II}L\cdot X_2]^{2-})_B$.

Evidence for an Inner-Sphere Mechanism. Direct evidence for the inner-sphere mechanism has been presented for the oxidation of $Co^{II}L^{2-}$ by bromine.[2] Due to the lability of the iron(III) complexes, the evidence that the $Fe^{II}L^{2-}$ oxidations proceed *via* an inner-sphere or outer-sphere mechanism is indirect. If both I_2 and I_3^- oxidized $Fe^{II}L^{2-}$ *via* an outer-sphere mechanism, electrostatic considerations would require that $\Delta S_2^{\ddagger}$ be more negative than $\Delta S_1^{\ddagger}$.[23] However, this is certainly not the case, and $\Delta S_2^{\ddagger}$ is positive while $\Delta S_1^{\ddagger}$ is negative for the iron reactions. Therefore, at least the I_3^- oxidation of $Fe^{II}L^{2-}$ (which is much slower than the I_2 oxidation) must be an inner-sphere reaction. Furthermore, comparison of the $\Delta S_2^{\ddagger}$ values to the activation entropies of substitution reactions of other $M^{II}L^{2-}$ species indicates that coordination of I_3^- is not the rate-determining step of this oxidation reaction. Reaction 8, which has similar reactants

$$Co^{II}(CyDTA)^{2-} + CN^- \rightarrow [Co^{II}(CyDTA)CN]^{3-} \qquad (8)$$

in structure charge type to $Fe^{II}L^{2-}$ and I_3^-, has an activation entropy of −29 eu.[28] This is quite inconsistent with the positive $\Delta S_2^{\ddagger}$ values for $Fe^{II}L^{2-}$. Moreover, the observed positive $\Delta S_2^{\ddagger}$ values correspond to the $\Delta S°$ value of +33 eu estimated[33] for reaction 9 but are inconsistent with the $\Delta S°$

$$Fe^{II}(CyDTA)^{2-} + I_3^- \rightarrow Fe^{III}(CyDTA)^- + I_2^- + I^- \qquad (9)$$

of −22 eu reported[28] for reaction 8. Hence the $Fe^{II}L^{2-}$-I_3^- reactions are thought to be controlled by the electron-transfer step.

If the fast (I_2, Br_2, and Br_3^-) oxidations of $Fe^{II}L^{2-}$ were outer-sphere reactions, the free energies of reaction would dictate that the Br_2 and I_2 rate constants be separated by several orders of magnitude.[3] However, the actual ratio of the Br_2:I_2 rates is only 8 which indicates that these reactions involve the rate of coordination of the oxidant in an inner-sphere oxidation. This ratio may reflect the relative steric hindrance of coordination of the halogens of differing size. The order of magnitude of the fast oxidations of $Fe^{II}L^{2-}$ ($10^7\ M^{-1}\ sec^{-1}$) probably represents the limiting rate at which a potential oxidant may enter the inner coordination sphere of $Fe^{II}L^{2-}$. The entropies of activation for the water-exchange reactions of $Ni^{II}(EDTA)^{2-}$ and $Mn^{II}(EDTA)^{2-}$ are −7 eu and +6.7 eu, respectively.[29,30] These values are consistent with a $\Delta S_1^{\ddagger}$ value of −5 eu for the $Fe^{II}L^{2-}$-I_2 reactions.

The question of whether the rate of the redox reaction may be limited by the rate of coordination of the oxidant does not arise for the $Co^{II}L^{2-}$ and $Mn^{II}L^{2-}$ reactions. The substitution reactions of $Co^{II}L^{2-}$ and $Mn^{II}L^{2-}$ are known[28,29]

---

(24) J. L. Hoard, C. H. L. Kennard, and G. S. Smith, *Inorg. Chem.*, 2, 1316 (1963).

(25) G. S. Smith and J. L. Hoard, *J. Amer. Chem. Soc.*, 81, 556 (1959).

(26) S. Richards, B. Pederson, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, 3, 27 (1964).

(27) G. H. Cohen and J. L. Hoard, *J. Amer. Chem. Soc.*, 88, 3228 (1966).

(28) J. P. Jones and D. W. Margerum, *Inorg. Chem.*, 8, 1486 (1969).

(29) M. S. Zetter, M. W. Grant, E. J. Wood, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 11, 2701 (1972).

(30) M. W. Grant, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 93, 6828 (1971).

(31) H. J. Schugar, A. T. Hubbard, F. C. Anson, and H. B. Gray, *J. Amer. Chem. Soc.*, 91, 71 (1969).

(32) N. A. Matwiyoff, C. E. Strouse, and L. O. Morgan, *J. Amer. Chem. Soc.*, 92, 5222 (1970).

(33) Present work and (for I_2^-) W. H. Woodruff and D. W. Margerum, *Inorg. Chem.*, 12, 962 (1973).

to be many orders of magnitude faster than the oxidation reactions observed here.

Details of the Oxidation Step. In the discussion to this point it has been assumed that the reactions investigated proceed *via* one-electron steps, but halogens may in principle function as two-electron oxidants. A choice must be made between a one-electron mechanism in which the post-rate-step reactive intermediate would be a halogen radical and a two-electron mechanism which would lead to the fleeting presence of $M^{IV}L$. In the case of the $Co^{II}L^{2-}$ oxidants, the one-electron mechanism has been demonstrated.[2] The one-electron mechanism remains an assumption for the iron and manganese reactions, but the assumption is supported by the comparable Marcus theory conformance of the metal centers (*vide infra*).

Another mechanistic possibility is that the k_{ox} steps (Chart I) may not represent true electron-transfer reactions but may instead be atom transfer reactions such as shown in eq 10 and 11. The argument which refutes the atom-transfer

$$[M^{II}L\cdot X_2]^{2-} \xrightarrow{\text{slow}} [M^{II}L\cdot X]^{2-} + X\cdot \qquad (10)$$

$$[M^{II}L\cdot X]^{2-} \xrightarrow{\text{rapid}} [M^{III}L\cdot X]^{2-} \qquad (11)$$

hypothesis is the same for iron as for cobalt.[2]

The Nature of the Postoxidation Step. It was previously suggested[1] that the rapid step, which followed the rate-determining one-electron reduction of iodine by $Fe^{II}(CyDTA)^{2-}$, was given by eq 12. It now appears that this can-

$$M^{II}L^{2-} + X_2^- \rightarrow M^{III}L^- + 2X^- \qquad (12)$$

not be the case, unless reaction 12 proceeds *via* an outer-sphere mechanism. We have seen that the coordination-controlled limiting rate for the $Fe^{II}L^{2-}$ oxidations is about 10^7 M^{-1} sec^{-1}, and this limit should apply equally to halogen radicals. Therefore reaction 12 (if inner-sphere) cannot be faster than the rapid oxidation by halogens of $Fe^{II}L^{2-}$, considering the expected ratio of halogen to halogen radical concentrations. However, the rate constants for halogen radical recombinations such as reaction 13 have been deter-

$$X_2^- + X_2^- \rightarrow X_2 + 2X^- \qquad (13)$$

mined[34,35] and are greater than 10^9 M^{-1} sec^{-1}. It is now thought that reaction 13 (or a similar reaction involving halogen atoms) represents the rapid postoxidation step in the oxidation of $Fe^{II}L^{2-}$ by halogens. Present data do not allow a choice between reactions 12 and 13 as the rapid step in the cobalt and manganese systems.

Marcus Theory Free Energy Relationships. The one-electron reduction of a halogen by a metal center is represented by eq 14. The corresponding self-exchange reactions are

$$M_{red} + X_2 \xrightarrow{k_{12}} M_{ox} + X_2^- \qquad (14)$$

given by eq 15 and 16. According to Marcus theory,[3] eq 17

$$M_{red} + M^*_{ox} \overset{k_{11}}{\rightleftarrows} M_{ox} + M^*_{red} \qquad (15)$$

$$X_2 + {}^*X_2^- \overset{k_{22}}{\rightleftarrows} X_2^- + X_2^* \qquad (16)$$

$$\Delta G_{12}^{\ddagger} = 0.5\Delta G_{11}^{\ddagger} + 0.5\Delta G_{22}^{\ddagger} + 0.5\Delta G_{12}^{\circ} - 0.5\,RT\ln f \qquad (17)$$

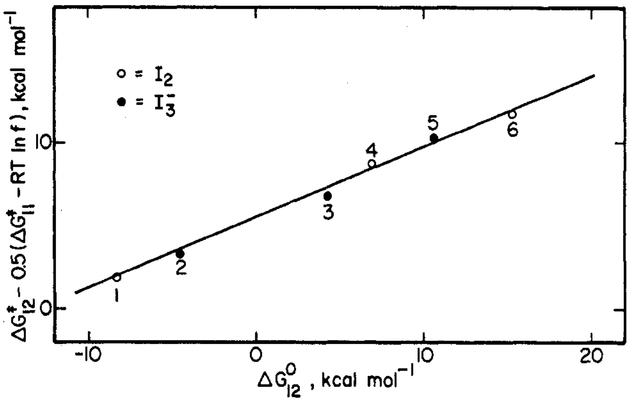


Figure 5. Marcus plot for the oxidation of bivalent metal centers by iodine. Reactant pairs are as follows: (1) $V^{2+}(aq)$, I_2; (2) $V^{2+}(aq)$, I_3^-; (3) $Fe^{II}EDTA^{2-}$, I_3^-; (4) $Co^{II}EDTA^{2-}$, I_2; (5) $Co^{II}EDTA^{2-}$, I_3^-, (6) $Fe^{3+}(aq)$, I_2 (estd).

gives the relationship among the free energies of activation for reactions 14–16 if outer-sphere mechanisms are followed and the work terms are small or cancel. More recently, Marcus has showed how[4] a relationship such as eq 17 could apply to strong-overlap electron-transfer reactions (*i.e.*, inner-sphere reactions), such as those studied in the present work. Other inner-sphere oxidations have shown a Marcus-type dependence of reactions rate on ΔG°.[36,37]

Other workers have investigated the oxidations of vanadium(II) by iodine and bromine[5] and of iron(II) by bromine[6] and the reduction of iodide ion by iron(III).[38,39] We have found that for a given halogen oxidant, with all these metal species, the reactions conform to the same Marcus-type free energy correlation and therefore it is possible to determine k_{22}. Table VIII gives the k_{11}, k_{12}, and ΔG_{12}° values for the reactions for which these correlations were drawn. According to eq 17, if $\Delta G_{12}^{\ddagger} - 0.5(\Delta G_{11}^{\ddagger} - RT\ln f)$ is plotted *vs.* ΔG_{12}°, a linear fit should result with a slope of 0.5 and an intercept (at $\Delta G_{12}^{\circ} = 0$) of $0.5\Delta G_{22}^{\ddagger}$. The definition of f is given in eq 18 where Z is 10^{11} M^{-1} sec^{-1}. An esti-

$$\ln f = \frac{(\Delta G_{12}^{\circ}/RT)^2}{4\ln(k_{11}k_{22}/Z^2)} \qquad (18)$$

mated k_{22} value is needed and an iterative procedure is used, but $RT\ln f$ is small and insensitive to the choice of the k_{22} value. Figure 5 presents such a plot for the oxidations by iodine and triiodide ion, and Figure 6 gives the same correlation for bromine and tribromide ion. The work term corrections are neglected considering the high ionic strength used. The slope of the line in Figure 5 is 0.43 ± 0.02 and the intercept is 5.4 ± 0.2 kcal mol^{-1}. In Figure 6 the slope is 0.45 ± 0.07 and the intercept is 7.7 ± 0.6 kcal mol^{-1}.

Marcus has discussed some reasons why the slope of such free energy correlations, for strong-overlap electron transfer, could deviate from a value of 0.5.[4] In general eq 17 remains valid except for the coefficient of ΔG_{12}°. Hence the intercepts of the free energy plots given here should represent $0.5\Delta G_{22}^{\ddagger}$. Therefore k_{22} for reaction 16, which cannot be measured directly in solution due to extremely rapid atom-transfer reactions,[34,35] can be evaluated from the intercepts of Figures 5 and 6. The nominal values of k_{22} (eq 16) which

---

(34) L. I. Grossweiner and M. S. Matheson, *J. Phys. Chem.*, **61**, 1089 (1957).

(35) A. T. Thornton and G. S. Laurence, *Chem. Commun.*, 443 (1970).

(36) N. Sutin and B. M. Gordon, *J. Amer. Chem. Soc.*, **83**, 70 (1961).

(37) A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **88**, 434 (1966).

(38) A. J. Fudge and K. W. Sykes, *J. Chem. Soc.*, 119 (1952).

(39) K. Srinivasan and G. A. Rechnitz, *Anal. Chem.*, **40**, 1955 (1968).

Table VIII. Self-Exchange and Cross-Reaction Data Used in Free Energy Correlations

Reactant pair	Metal^{II,III} self-exchange k_{11},[a] M^{-1} sec^{-1}	k_{12},[a] M^{-1} sec^{-1}	One-electron $\Delta G_{12}°$,[b] kcal mol^{-1}
V^{2+}(aq), Br_2	1.0×10^{-2} [c]	3.1×10^4 [d] ($\mu = 1.0$)	−17.6
V^{2+}(aq), I_2	1.0×10^{-2} [c]	7.5×10^3 [d] ($\mu = 1.0$)	−8.4
V^{2+}(aq), I_3^-	1.0×10^{-2} [c]	9.7×10^2 [d] ($\mu = 1.0$)	−4.5
$Co^{II}EDTA^{2-}$, $(X_2)_T$	4.0×10^{-7} [e]	[f] ($\mu = 1.1$)	[f]
$Fe^{II}EDTA^{2-}$, I_3^-	3.0×10^4 [g]	[f] ($\mu = 0.2$)	[f]
$Mn^{II}EDTA^{2-}$, $(Br_2)_T$	1.2[g]	[f] ($\mu = 1.1$)	[f]
Fe^{2+}(aq), Br_2	3.7[h]	0.76[i] ($\mu = 1.0$)	7.1
Fe^{2+}(aq), I_2	3.7[h]	5×10^{-3} [j] ($\mu = 1.0$)	15.3

[a] Equations 14, 15. [b] See footnote *a*, Table VII. [c] K. V. Krishnamurthy and A. C. Wahl, *J. Amer. Chem. Soc.*, **80**, 5921 (1958). [d] Reference 5. [e] R. G. Wilkins and R. E. Yelin, *Inorg. Chem.*, 7, 2667 (1968). [f] Tables VI and VII. [g] Y. A. Im and D. H. Busch, *J. Amer. Chem. Soc.*, **83**, 3357 (1961). [h] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952). [i] Reference 6. [j] Estimated from data in ref 38 and 39.

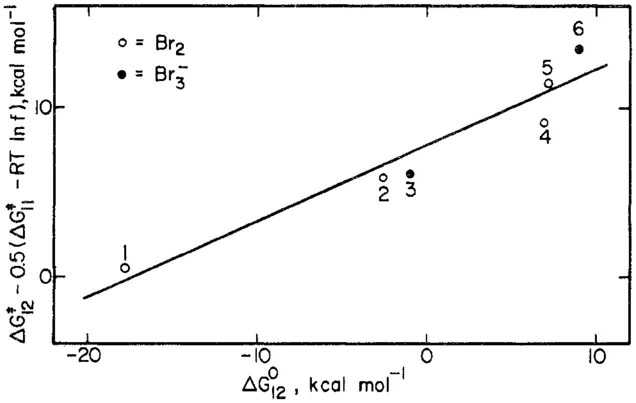


Figure 6. Marcus plot for the oxidation of bivalent metal centers by bromine. Reactant pairs are as follows: (1) V^{2+}(aq), Br_2; (2) $Co^{II}EDTA^{2-}$, Br_2; (3) $Co^{II}EDTA^{2-}$, Br_3^-; (4) Fe^{2+}(aq), Br_2; (5) $Mn^{II}EDTA^{2-}$, Br_2; (6) $Mn^{II}EDTA^{2-}$, Br_3^-.

are calculated are 8.5×10^4 M^{-1} sec^{-1} for iodine and 29 M^{-1} sec^{-1} for bromine.

The force constant of the X–X bond in Br_2 is 1.42 times that in I_2, and the force constant in Br_2^- is 1.07 times that in I_2^-.[40] The difference in bond length between X_2 and X_2^- is about 0.5 Å for each halogen.[40] The primary difference in the activation free energy of reaction 16, between X = I and Br, probably lies in the energy necessary to stretch the X–X bond in X_2 prior to electron transfer. Considering this, and the force constant ratios quoted above, it is not surprising that reaction 16 is slower when X is Br than when X is I.

The data for both the X_2 and X_3^- oxidations are plotted in Figures 5 and 6 and it appears that the self-exchange rate constants under the conditions used are not significantly different for X_2-X_2^- compared to X_3^--X_3^{2-}. However, a source of error in these plots is that the $\Delta G_{12}°$ for X_3^- is based on eq 9 because the $\Delta G°$ of X_3^{2-} is unknown.

It is evident from Figures 5 and 6 that the immense differences in rate between the iron and cobalt systems studied in this work are primarily due to the differences between the k_{11} values for the two metal complexes. The sluggishness of self-exchange reactions of cobalt complexes with intermediate-field ligands has been attributed[41] to the spin-forbidden nature of the $t_{2g}^5e_g^2$, t_{2g}^6 exchange involved. However, it has been recently proposed[42] that the slow exchange may be due to a reorganizational barrier created by Jahn–Teller distortion after spin pairing of Co^{II} complexes.

The activation parameters given in Table VI show that the $\Delta S_2^{\ddagger}$ values for the Fe^{II} reactions are much larger than those for the Co^{II} reactions. The reaction in eq 9 has an estimated $\Delta S°$ of +33 eu for Fe^{II} and the corresponding Co^{II} reaction should be similar. On this basis the $\Delta S_2^{\ddagger}$ values for Fe^{II} are consistent with $\Delta S°$ while the $\Delta S_2^{\ddagger}$ values for Co^{II} are much more negative. It is conceivable that the transmission coefficient is much less than unity for the spin-forbidden transition discussed above for cobalt. If this were the case it would cause the experimental $\Delta S^{\ddagger}$ values to be more negative than the true values. However, the $\Delta S^{\ddagger}$ value for the pseudoexchange of $Fe^{II}(EDTA)^{2-}$ with $Fe^{III}(CyDTA)^-$ is −25 eu[43] which is nearly the same as the $\Delta S^{\ddagger}$ value of −21 eu for the self-exchange of $Co^{II}(EDTA)^{2-}$-$Co^{III}(EDTA)^-$.[44] Hence it does not appear to be valid to assign the differences in activation entropy to a small transmission coefficient for the cobalt reaction.

As noted above, the $\Delta S_2^{\ddagger}$ value for the $Fe^{II}L^{2-}$ reaction is similar to the large positive $\Delta S°$ value for reaction 9. On the other hand the $\Delta S_2^{\ddagger}$ value for the $Co^{II}L^{2-}$ reaction is negative and this is also the case for the substitution reaction in eq 8. It therefore appears that the transition state for the electron-transfer reaction is closer to reaction products for the iron system than it is for the cobalt system. The negative $\Delta S_2^{\ddagger}$ for cobalt indicates that the structure of the transition state for this metal is closer to that of the inner-sphere cobalt(II) intermediate complex. This is consistent with the proposed mechanism in which the cobalt system must form a six-coordinate inner-sphere intermediate while the iron system can react in an expanded coordination geometry. Accordingly the large $\Delta H_2^{\ddagger}$ value for the iron system reflects extensive reorganization of internuclear coordinates to a configuration resembling products. On the other hand, the high $\Delta H^{\ddagger}$ values for the cobalt systems reflect displacement of a coordinated group and perhaps a reorganizational barrier due to Jahn–Teller distortion in spin-paired cobalt(II).

Conclusions

Despite the very large differences in the rates of the reactions studied, a general mechanism may be written which accounts for the observed kinetics. The rate-determining process within the general mechanism is not the same for all reactant pairs studied. It is the substitution step for some reactions and an electron-transfer step for others. Although the latter group of reactions are inner-sphere and involve a nonmetallic oxidizing agent, the reactions conform to the modified Marcus theory. Furthermore, other systems studied by previous workers fit the free energy correlations made for the reactions in the present study. These correlations include a total of four bivalent metals and five different reducing agents (V^{2+}(aq), Fe^{2+}(aq), $Fe^{II}L^{2-}$, $Co^{II}L^{2-}$, and $Mn^{II}L^{2-}$).

---

(40) W. B. Person, *J. Chem. Phys.*, 33, 109 (1963).

(41) A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, 10, 168 (1967).

(42) M. D. Glick, J. M. Kuszaj, and J. F. Endicott, *J. Amer. Chem. Soc.*, 95, 5097 (1973).

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

(44) Y. A. Im and D. H. Busch, *J. Amer. Chem. Soc.*, 83, 3357 (1961).

Values are calcualted for the one-electron self-exchange rate constants of Br_2, Br_2^- and I_2, I_2^-. Knowledge of these self-exchange rate constants should allow the prediction of the rates of other electron-transfer reactions involving these halogens. An immediate example is the prediction that the reaction of $Cr^{II}EDTA^{2-}$ with I_2 should be very fast and either diffusion or substitution controlled.

Acknowledgment. This investigation was sponsored by the Air Force Office of Scientific Research under AFOSR Grant 71-1988.

Registry No. $Fe^{II}(EDTA)^{2-}$, 15651-72-6; I_2, 7553-56-2; I_3^-, 14900-04-0; $Fe^{II}(CyDTA)^{2-}$, 34446-90-7; Br_2, 7726-95-6; Br_3^-, 14522-80-6; $Mn^{II}(EDTA)^{2-}$, 52279-49-9; $Fe^{III}(CyDTA)^-$, 52305-99-4.

Contribution from the Biophysics Research Laboratory, Department of Biological Chemistry,
Harvard Medical School, Division of Medical Biology, Peter Bent Brigham Hospital, Boston, Massachusetts 02115

Magnetic Circular Dichroism of Cobalt(II) Complexes

THOMAS A. KADEN,[1] BARTON HOLMQUIST, and BERT L. VALLEE*

Received February 1, 1974 AIC40074Y

Absorption and magnetic circular dichroic (MCD) spectra of d → d transitions of hexa-, penta-, and tetracoordinate high-spin Co(II) complexes have been measured and their zeroth and first moments determined. Octahedral complexes exhibit a single major negative MCD band at a frequency corresponding to that of their absorption maxima. Tetrahedral complexes display a strong negative and a weaker positive band. The MCD spectra of pentacoordinate complexes of various geometries consist of several negative and, in some instances, an additional positive band. *B* and *C* components of the zeroth moment have also been differentiated through measurements of the temperature dependence of the absorption and MCD spectra of $CoSO_4$ in water–ethylene glycol and of $Co(py)_2Br_2$ and $Co(Et_4dien)Cl_2$ in Plexiglas. These complexes exemplify both the three coordination geometries considered and the three classes of MCD spectra observed. The results obtained indicate that each type of coordination generates a characteristic MCD spectrum which appears to be rather insensitive both to distortions of the coordination sphere of the metal ion and to the presence of chelate rings, each of which lower the symmetry of the complex. MCD seems to provide an additional and important method to classify and predict the overall structure of Co(II) complexes.

Introduction

The coordination geometry of many simple Co(II) complexes has been determined on the basis of spectral,[2a] epr,[2b] and magnetic[3] measurements; however, frequently such determinations have proven difficult for Co(II) complexes liganded with bulky or rigid groups or for Co(II)-substituted metalloenzymes.[4] Recent instrumental developments and theoretical advances[5,6] have suggested that MCD might provide an additional approach to study the structure of such metal complexes. The magnetic circular dichroic spectra of $Co(H_2O)_6^{2+}$,[7,8] $CoCl_4^{2-}$, $CoBr_4^{2-}$, and CoI_4^{2-},[9] have been described previously, and a detailed calculation on the MCD of $CoCl_4^{2-}$ and its temperature dependence has been published.[10] MCD measurements on $CoCl_4^{2-}$ in Cs_3ZnCl_5 have also been used to detect weak bands due to spin-forbidden transitions.[11] We have now examined the MCD spectra of Co(II) complexes of known structures for comparison with those of analogous complexes where the structure is thus far unknown.

Experimental Section[12]

Me_6tren,[13] POA,[14] $Co(Me_6tren)Br_2$,[13] $Co(Et_4dien)Cl_2$,[15] $Co(terpy)Cl_2$,[16] $Co(DPVM)_2$,[17] and $Co(py)_2Br_2$[18] were synthesized as described in the literature. All other complexes were made by mixing appropriate solutions of the ligand with either $CoSO_4$ or $Co(NO_3)_2$ at the desired pH.

The experimental conditions for the solutions used to measure the absorption and MCD spectra are as follows: $Co(H_2O)_6^{2+}$, 5.0×10^{-2} *M* $CoSO_4$ in water;[19] $Co(DMSO)_6^{2+}$, 5.0×10^{-2} *M* $Co(NO_3)_2$ in DMSO;[20] $Co(NH_3)_6^{2+}$, 5.0×10^{-2} *M* $Co(NO_3)_2$ in 6 *M* NH_3;[19] $Co(trien)(H_2O)_2^{2+}$, 1.0×10^{-1} *M* $CoSO_4$ in 2.0×10^{-1} *M* trien at pH 8;[21] $Co(trien)(H_2O)OH^+$, 1.5×10^{-2} *M* $CoSO_4$ in 2.0×10^{-1} *M* trien at pH >13;[21] $Co(glygly)_2$, 3.3×10^{-2} *M* $CoSO_4$ in 2.0×10^{-1} *M* glygly at pH 9 and $Co(glyglyH_{-1})_2^{2-}$ at pH >13;[22] $Co(OH)_4^{2-}$, 3.2×10^{-3} *M* $CoSO_4$ in 50% NaOH;[23] $Co(SCN)_4^{2-}$, 5.0×10^{-2} *M* $CoSO_4$ with 0.1 *M* KSCN in acetone;[24] $Co(DPVM)_2$, 1.6×10^{-2} *M*

(1) On leave from the University of Basel; supported by the Swiss Foundation for Fellowships in Chemistry.

(2) (a) A. Lever, "Inorganic Electronic Spectroscopy," Elsevier, New York, N. Y., 1968, p 317; R. L. Carlin, *Transition Metal Chem.*, 1, 1 (1965); (b) H. L. Schlafer and G. Gliemann, "Einfuhrung in die Ligandfeldtheorie," Akademische Verlagsgesellshaft, Frankfurt am Main, 1967, p 144.

(3) B. R. McGarvey, *Transition Metal Chem.*, 3, 176 (1966).

(4) B. L. Vallee, S. A. Latt, and R. J. P. Williams, *Proc. Nat. Acad. Sci. U. S.*, 59, 498 (1968).

(5) A. D. Buckingham and P. J. Stephens, *Annu. Rev. Phys. Chem.*, 17, 399 (1966); P. M. Schatz and A. J. McCaffery, *Quart. Rev., Chem. Soc.*, 23, 552 (1969).

(6) P. J. Stephens, *J. Chem. Phys.*, 52, 3489 (1970).

(7) A. J. McCaffery, P. J. Stephens, and P. M. Schatz, *Inorg. Chem.*, 6, 1614 (1967), and references therein.

(8) M. J. Harding and B. Briat, *Mol. Phys.*, 25, 745 (1973).

(9) R. G. Denning, *J. Chem. Phys.*, 45, 1307 (1966).

(10) R. G. Denning and J. A. Spencer, *Symp. Faraday Soc.*, 3, 84 (1969).

(11) T. A. LoMenzo, B. D. Bird, G. A. Osborne, and P. J. Stephens, *Chem. Phys. Lett.*, 3, 332 (1971).

(12) Abbreviations used: Me_6tren; tris(2-dimethylaminoethyl)amine; POA, *N*-2-picolyloxamide; Et_4dien, *N,N,N',N'*-tetraethyldiethylenetriamine; terpy, 2,2':6',2''-terpyridine; DPVM, dipivaloylmethane; py, pyridine; trien, triethylenetetramine; glygly, glycylglycine; his, histidine; DMSO, dimethyl sulfoxide.

(13) M. Ciampolini and N. Nardi, *Inorg. Chem.*, 5, 41 (1966).

(14) P. Donatsch, A. Zuberbuhler, and S. Fallab, *Experientia*, 26, 1185 (1970).

(15) Z. Dori and H. B. Gray, *Inorg. Chem.*, 7, 889 (1968).

(16) R. Hogg and R. G. Wilkins, *J. Chem. Soc. A*, 341 (1962).

(17) F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, 3, 1 (1964).

(18) A. B. P. Lever and S. M. Nelson, *J. Chem. Soc. A*, 859 (1966).

(19) C. K. Jorgensen, *Advan. Chem. Phys.*, 5, 33 (1963).

(20) H. Schlafer and H. P. Opitz, *Z. Elektrochem.*, 65, 372 (1961).

(21) F. Miller and R. G. Wilkins, *J. Amer. Chem. Soc.*, 92, 2687 (1970).

(22) M. S. Michailidis and R. B. Martin, *J. Amer. Chem. Soc.*, 91, 4683 (1969).

(23) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, 83, 4690 (1961).

(24) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Amer. Chem. Soc.*, 83, 4157 (1961).