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Kinetics of Oxidation of Cobalt(II) Complexes of Ethylenediaminetetraacetate and Cyclohexylenediaminetetraacetate by Halogens

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The rate of oxidation of $Co^{II}L^{2-}$ complexes, where L is $EDTA^{4-}$ or $CyDTA^{4-}$ (*trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetate), by iodine or bromine is first order in $Co^{II}L^{2-}$ and first order in total halogen ($X_2 + X_3^-$). The resolved rate constants (M^{-1} sec^{-1} at 25°) for the EDTA complex are 5.2×10^{-4} for I_2, 3.1×10^{-5} for I_3^-, 7.3×10^{-2} for Br_2, and 5.4×10^{-2} for Br_3^-. Those for the CyDTA complex are 6.4×10^{-5} for I_2, 2.2×10^{-5} for I_3^-, 2.0×10^{-3} for Br_2, and 1.1×10^{-3} for Br_3^-. The reactions follow an inner-sphere electron-transfer mechanism which takes place in one-electron steps. Steric effects in the aminocarboxylate ligand account for the generally smaller rate constants for $Co^{II}(CyDTA)^{2-}$ compared to $Co^{II}(EDTA)^{2-}$ with given oxidants. The $\Delta H^{\ddagger}$ values are smaller for bromine than for the iodine reactions but are similar for X_2 and X_3^-. The $\Delta S^{\ddagger}$ values are negative for both the I_3^- and Br_3^- reactions with $Co^{II}(CyDTA)^{2-}$.

Introduction

An earlier report from these laboratories[1] described the kinetics of the oxidation of $Fe^{II}(CyDTA)^{2-}$ by iodine and triiodide ion. The rate of oxidation by I_2 is fast (the second-order rate constant is 1.24×10^6 M^{-1} sec^{-1} at 25.0°). The I_3^- rate is 250 times slower than the I_2 rate at 25° but the activation entropy for the I_3^- oxidation is unusually positive. In the present study the reactions under investigation are given in eq 1, where L is $EDTA^{4-}$ or $CyDTA^{4-}$ and

$$2Co^{II}L^{2-} + \begin{bmatrix} X_2 + X^- \\ \uparrow\downarrow \\ X_3^- \end{bmatrix} \rightarrow 2Co^{III}L^- + 3X^- \qquad (1)$$

X is iodine or bromine. These cobalt reactions are eight to ten orders of magnitude slower than the corresponding reactions of $Fe^{II}L^{2-}$. Individual rate constants are resolved for the X_2 and X_3^- reactions. With the cobalt(II) complexes the X_3^- ion is only 1.3-16.7 times slower to react than X_2, in contrast to the iron(II) system. The activation entropies for I_3^- and Br_3^- are negative for the $Co^{II}(CyDTA)^{2-}$ reaction whereas the $\Delta S^{\ddagger}$ for the I_3^- reaction with $Fe^{II}(CyDTA)^{2-}$ is large and positive. In a subsequent report[2] additional comparisons of metal centers and ligands provide a basis for development of a general mechanism for reactions of this type. The present paper concerns the mechanism of the Co^{II} oxidations and the effects of bromine *vs.* iodine and of CyDTA *vs.* EDTA.

Experimental Section

Reagents and Materials. The sodium salts of $Co^{II}L^{2-}$ (L = EDTA, CyDTA) were prepared by a modification of the method of Schwarzenbach and Parissakis.[3] In the present preparation, 0.2 mol each of reagent grade H_4L and $CoCO_3$ were stirred together in 400 ml of H_2O. When CO_2 evolution ceased, the solution was neutralized with solid NaOH and filtered. The filtrate was evaporated on a steam table until crystals appeared on the surface of the solution and then cooled to room temperature. The product was precipitated by slowly adding 600 ml of absolute methanol, filtered, and then dried overnight in a vacuum oven at 100°. Good microanalyses were obtained for $Na_2Co^{II}CyDTA \cdot 3H_2O$ and $Na_2Co^{II}EDTA \cdot 2H_2O$.

Reagent grade sodium perchlorate was recrystallized twice before use. Cesium triiodide, obtained from Alfa Inorganics (Beverly, Mass.), was the source of iodine for the $Co^{II}L^{2-}$ oxidations. The purity of this reagent was confirmed titrimetrically. All other chemicals were reagent grade, used without further purification.

Bromine solutions were prepared from elemental bromine and just prior to use were standardized spectrophotometrically at the isosbestic point of Br_2 and Br_3^- (λ 457 nm, ϵ 98 M^{-1} cm^{-1}).

Instrumentation. Reactions were followed using either a Cary 16 spectrophotometer interfaced to a Varian G-2000 recorder or a Cary 14 spectrophotometer. Absorbance–time data were normally taken from the recorder chart, although for some experiments data were taken on-line with a Hewlett-Packard 2115A computer as described elsewhere.[4] Measurements of pH were made using an Instrumentation Laboratory 245 pH meter with a reference electrode containing saturated NaCl.

Results

General Data. All of the reactions studied were first order in total halogen concentration and first order in cobalt(II) chelate concentration. The rate constants due to the reactions of molecular halogen and of trihalide ion were resolved by evaluating the second-order rate constant at various total halide ion concentrations. This second-order rate constant is designated k_0 throughout this work and is defined such that $-d([X_2]_T)/dt = k_0[X_2]_T[Co^{II}L^{2-}]$, where $[X_2]_T = [X_2] + [X_3^-]$.

The hydrolysis of bromine to hypobromous acid is a potential interference in the study of bromine reactions. It has been found[5] that the rates of oxidation of cobalt(II) complexes of EDTA and CyDTA are two to three orders of magnitude faster with HOBr than with Br_2. In the present study, pH and bromide ion concentrations were chosen such that the HOBr reaction was negligible.

The notation used to identify the rate constants due to X_2 and X_3^- is

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

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

with the reaction designated by k_n having activation parameters $\Delta H_n^{\ddagger}$ and $\Delta S_n^{\ddagger}$. Linear least-squares methods were employed both for the resolution of k_1 and k_2 (using the equations previously developed[1]) and for determination of the activation parameters. Error limits of the resolved rate constants and the activation parameters are the standard deviations of these least-squares fits.

$Co^{II}L^{2-}$-Bromine Reactions. First-order behavior in both $Co^{II}L^{2-}$ and bromine was confirmed for these systems by carrying out separate reactions with first one and then the

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

(2) W. H. Woodruff and D. W. Margerum, *Inorg. Chem.*, **13**, 2578 (1974).

(3) G. Schwarzenbach and G. Parissakis, *Helv. Chim. Acta*, **41**, 2425 (1958).

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

(5) W. H. Woodruff, D. W. Margerum, M. J. Milano, H. L. Pardue, and R. E. Santini, *Inorg. Chem.*, **12**, 1490 (1973).

Table I. Kinetics Data for the Oxidation of $Co^{II}L^{2-}$ by Bromine[a]

Temp, °C	$[Br^-]_T, M$	$[Br_2]_T, M$	$10^3k_0, M^{-1}\ sec^{-1}$
	L = CyDTA		
25.0	0.040	0.018	1.53
25.0	0.080	0.036	1.50
25.0	0.540	0.018	1.30
25.0	0.580	0.035	1.15
25.0	1.040	0.018	1.14
40.3	0.080	0.034	7.46
40.3	0.580	0.034	5.67
40.3	1.080	0.032	5.45
54.9	0.040	0.016	31.0
54.9	0.540	0.016	21.8
54.9	1.040	0.016	20.7
	L = EDTA		
25.0	0.120	7.8×10^{-3}	59.4
25.0	0.520	7.8×10^{-3}	56.8
25.0	1.020	7.8×10^{-3}	55.1

[a] $\mu = 1.1$ ($NaClO_4$ + NaBr), pH 3.5–4 (0.1 *M* acetate buffer), $[Co^{II}L^{2-}] = 1.00 \times 10^{-3}\ M$ except at 54.9°, where $[Co^{II}CyDTA^{2-}] = 5.00 \times 10^{-4}\ M$.

other reactant in excess. Thereafter, the kinetic runs were performed under first-order conditions with bromine in excess. The values of k_0 were calculated from the apparent first-order rate constants, k_{app}, by the relationship $k_0 = k_{app}/2[Br_2]_T$. Solutions containing bromine, sodium bromide, and sodium perchlorate were mixed with those containing $Co^{II}L^{2-}$, acetate buffer, sodium perchlorate, and if necessary sodium bromide. The reactions were monitored at 540 nm for L = CyDTA and at either 540 or 590 nm (λ_{max} for $[Co^{III}(EDTA)Br]^{2-}$) for L = EDTA. The rates are independent of acidity for the pH range (3.0–4.0) used.

Earlier workers[6,7] have observed that the initial product of the oxidation of $Co^{II}EDTA^{2-}$ by bromine is $[Co^{III}(EDTA)Br]^{2-}$. This is also the case in the present work. The observed product of the oxidation of $Co^{II}CyDTA^{2-}$ by bromine is $Co^{III}CyDTA^-$. This is in accord with the expectation that $[Co^{III}(CyDTA)Br]^{2-}$ expels bromide ion much faster than $[Co^{III}(EDTA)Br]^{2-}$. The elimination of chloride from $[Co^{III}(CyDTA)Cl]^{2-}$ is 5000 times faster than from $[Co^{III}(EDTA)Cl]^{2-}$ [8,9] and the ring closure of $[Co^{III}(CyDTA)OH]^{2-}$ is 10^4 times faster than that of $[Co^{III}(EDTA)OH]^{2-}$.[5] When the oxidation of $Co^{II}CyDTA^{2-}$ is accelerated by using higher concentrations of bromine, $[Co^{III}(CyDTA)Br]^{2-}$ is detected as a product. Thus, the kinetic data reported here refer to the same oxidative process whether L = EDTA or CyDTA.

The observed kinetics data for the oxidation of $Co^{II}L^{2-}$ by bromine are presented in Table I and resolved as shown in Figures 1 and 2. The values of k_1 and k_2 at each temperature are given in Table II. The data of Scaife and Tyrrel[10] were used for the temperature dependence of the stability constant of Br_3^-.

During the study of the oxidation of $Co^{II}EDTA^{2-}$, the dissociation reaction of the initial product

$$[Co^{III}(EDTA)Br]^{2-} \rightarrow Co^{III}EDTA^- + Br^- \qquad (4)$$

also was observed. Reaction 4 is accelerated by the presence of bromine.[11] Conditions were adjusted so that reaction 4 did not interfere with the present oxidation measurements.

$Co^{II}L^{2-}$-Iodine Reactions. These reactions were observed

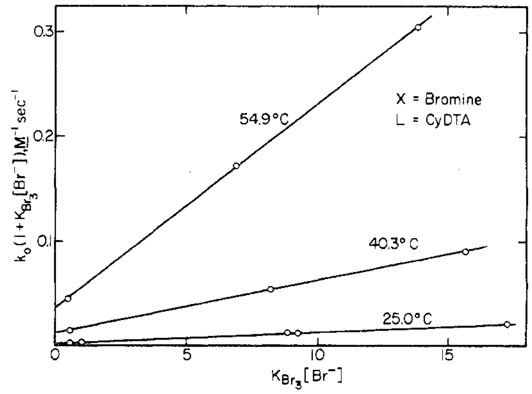

Figure 1. Plot of data used to resolve k_1 (intercept) and k_2 (slope) for the oxidation of $Co^{II}(CyDTA)^{2-}$ by $[Br_2]_T$ at the temperatures studied.

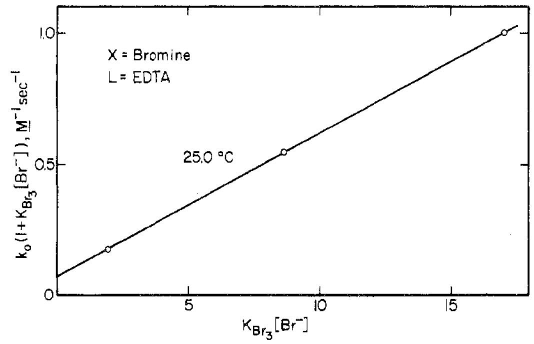

Figure 2. Plot of data used to resolve k_1 (intercept) and k_2 (slope) for the oxidation of $Co^{II}(EDTA)^{2-}$ by $[Br_2]_T$ at 25.0°.

Table II. Resolved Rate Constants for the Reactions of Br_2 and Br_3^- with $Co^{II}L^{2-}$ ($\mu = 1.1$)

Temp, °C	K_{Br_3}, M^{-1}	$k_1, M^{-1}\ sec^{-1}$	$k_2, M^{-1}\ sec^{-1}$
		L = CyDTA	
25.0	16.85	$(2.0 \pm 0.4) \times 10^{-3}$	$(1.11 \pm 0.05) \times 10^{-3}$
40.3	14.9	$(9.6 \pm 0.2) \times 10^{-3}$	$(5.18 \pm 0.05) \times 10^{-3}$
54.9	13.5	$(3.67 \pm 0.07) \times 10^{-2}$	$(1.96 \pm 0.01) \times 10^{-2}$
		L = EDTA	
25.0	16.85	$(7.3 \pm 0.8) \times 10^{-2}$	$(5.42 \pm 0.07) \times 10^{-2}$

Table III. Rate Constants from Integrated Rate Expressions for the Oxidation of $Co^{II}L^{2-}$ by Iodine[a]

Temp, °C	$[Co^{II}L^{2-}], M$	$[(I_2)_T]_0, M$	$[I^-], M$	$k_0, M^{-1}\ sec^{-1}$
		L = CyDTA		
25.0	5.00×10^{-3}	1.00×10^{-3}	0.050	2.3×10^{-5}
25.0	5.00×10^{-3}	1.00×10^{-3}	0.100	2.0×10^{-5}
25.0	1.00×10^{-2}	5.00×10^{-4}	0.050	2.9×10^{-5}
25.0	1.00×10^{-2}	5.00×10^{-4}	0.100	2.3×10^{-5}
55.5	5.00×10^{-3}	1.00×10^{-3}	0.050	6.6×10^{-4}
55.5	5.00×10^{-3}	1.00×10^{-3}	0.100	6.4×10^{-4}
55.5	1.00×10^{-2}	5.00×10^{-4}	0.050	5.6×10^{-4}
55.5	1.00×10^{-2}	5.00×10^{-4}	0.100	5.5×10^{-4}
71.5	1.00×10^{-2}	5.12×10^{-4}	0.050	3.6×10^{-3}
71.5	1.00×10^{-2}	5.00×10^{-4}	0.100	3.4×10^{-3}
		L = EDTA		
25.0	5.00×10^{-3}	1.00×10^{-3}	0.050	5.4×10^{-5}
25.0	1.00×10^{-2}	5.20×10^{-4}	0.050	5.1×10^{-5}
25.0	1.00×10^{-2}	1.00×10^{-3}	0.100	3.6×10^{-5}
41.0	1.00×10^{-2}	5.08×10^{-4}	0.050	4.3×10^{-4}
41.0	1.00×10^{-2}	5.08×10^{-4}	0.100	2.3×10^{-4}
52.5	1.00×10^{-2}	5.00×10^{-4}	0.100	2.1×10^{-3}
54.5	1.00×10^{-2}	5.00×10^{-4}	0.050	3.2×10^{-3}
71.5	1.00×10^{-2}	5.00×10^{-4}	0.050	1.7×10^{-2}
71.5	1.00×10^{-2}	5.00×10^{-4}	0.100	1.3×10^{-2}

[a] $\mu = 1.0$ ($NaClO_4$), pH 5–6 (unbuffered).

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(6) G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).
(7) A. W. Adamson, *Recl. Trav. Chim. Pays-Bas*, **75**, 809 (1956).
(8) R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, 1998 (1960).
(9) B. Grossman, Ph.D. Thesis, State University of New York at Buffalo, 1969.
(10) D. B. Scaife and H. J. V. Tyrrel, *J. Chem. Soc.*, 386 (1958).
(11) W. H. Woodruff and D. W. Margerum, *Inorg. Chem.*, **12**, 958 (1973).

Table IV. Kinetics Data from Initial Rates for the Oxidation of $Co^{II}L^{2-}$ by Iodine[a]

Temp, °C	$[Co^{II}L^{2-}]$, M	$[CsI_3]_0$, M	Av $[I_2]_T$, M	Av $[I^-]$, M	k_0, M^{-1} sec^{-1}
L = CyDTA					
25.0	1.00×10^{-2}	5.00×10^{-4}	4.8×10^{-4}	4.3×10^{-4}	6.2×10^{-5}
24.9	2.00×10^{-2}	1.00×10^{-3}	9.9×10^{-4}	6.9×10^{-4}	4.2×10^{-5}
37.1	2.00×10^{-2}	5.00×10^{-4}	4.9×10^{-4}	4.4×10^{-4}	2.4×10^{-4}
37.1	2.00×10^{-2}	1.00×10^{-3}	9.9×10^{-4}	7.6×10^{-4}	2.2×10^{-4}
37.1	1.00×10^{-2}	5.00×10^{-4}	4.8×10^{-4}	4.5×10^{-4}	2.5×10^{-4}
54.3	5.00×10^{-3}	1.00×10^{-3}	9.8×10^{-4}	8.1×10^{-4}	1.5×10^{-3}
54.3	1.00×10^{-2}	5.00×10^{-4}	4.8×10^{-4}	4.7×10^{-4}	1.6×10^{-3}
L = EDTA					
25.0	1.00×10^{-2}	5.00×10^{-4}	4.8×10^{-4}	4.3×10^{-4}	4.1×10^{-4}
25.0	2.00×10^{-2}	1.00×10^{-3}	9.9×10^{-4}	6.9×10^{-4}	3.5×10^{-4}
37.2	1.00×10^{-2}	1.00×10^{-3}	9.9×10^{-4}	7.6×10^{-4}	1.0×10^{-3}
37.1	2.00×10^{-2}	5.00×10^{-4}	4.9×10^{-4}	4.4×10^{-4}	1.8×10^{-3}
41.8	1.00×10^{-2}	5.00×10^{-4}	4.9×10^{-4}	4.4×10^{-4}	2.5×10^{-3}
54.3	2.00×10^{-3}	5.00×10^{-4}	4.8×10^{-4}	4.8×10^{-4}	8.7×10^{-3}
54.2	4.00×10^{-3}	2.50×10^{-4}	2.4×10^{-4}	2.5×10^{-4}	7.3×10^{-3}

[a] $\mu = 1.0$ ($NaClO_4$), pH 5-6 (unbuffered).

Table V. Resolved Rate Constants for the Reactions of I_2 and I_3^- with $Co^{II}L^{2-}$

Temp, °C	K_{I_3},[a] M^{-1}	k_1,[b] M^{-1} sec^{-1}	Intercepts of Figures 3 and 4, M^{-1} sec^{-1}	k_2,[c] M^{-1} sec^{-1}
L = CyDTA				
25.0 ± 0.1	768	$(6.4 \pm 1.1) \times 10^{-5}$	$(8.7 \pm 5.5) \times 10^{-5}$	$(2.2 \pm 0.1) \times 10^{-5}$
37.1 ± 0.1	550	$(2.8 \pm 0.3) \times 10^{-4}$		7.6 ± 10^{-5} [d]
55.1 ± 0.5	354	$(1.8 \pm 0.2) \times 10^{-3}$	$(1.7 \pm 0.2) \times 10^{-3}$	$(5.63 \pm 0.08) \times 10^{-4}$
71.5 ± 0.5	235		9.0×10^{-3}	3.2×10^{-3}
L = EDTA				
25.0 ± 0.1	768	$(5.2 \pm 0.1) \times 10^{-4}$	$(5.9 \pm 1.8) \times 10^{-4}$	$(3.1 \pm 0.4) \times 10^{-5}$
37.1 ± 0.1	550	$(1.8 \pm 0.4) \times 10^{-3}$		1.5×10^{-4} [d]
41.3 ± 0.4	488	$(3.1 \pm 0.3) \times 10^{-3}$	$(4.2 \pm 2.7) \times 10^{-4}$	$(1.7 \pm 0.9) \times 10^{-4}$
53.9 ± 0.7	358	$(8.7 \pm 0.9) \times 10^{-3}$	$(1.1 \pm 0.7) \times 10^{-2}$	$(2.0 \pm 0.4) \times 10^{-3}$
71.5 ± 0.5	235		0.11	8.7×10^{-3}

[a] From data of A. D. Autrey and R. E. Connick, *J. Amer. Chem. Soc.*, **73**, 1842 (1951); M. Davies and E. Gwynne, *ibid.*, 74, 2748 (1952); and G. Daniele, *Gazz. Chim. Ital.*, 90, 1068 (1960). [b] Calculated from initial-rate k_0 values and k_2 values in last column, this table. [c] Slopes of Figures 3 and 4, unless otherwise noted. [d] Estimated from k_2 activation parameters.

under first-order and under second-order conditions and by the method of initial rates. The initial rate measurements were possible because of the sluggishness of the iodine oxidations and were desirable in order to evaluate k_0 at low iodide ion concentrations ($[I^-] < [I_2]_T$). In the reactions which were run under first-order or second-order conditions, iodide ion was present in large excess over total iodine. Solutions containing CsI_3, NaI, and $NaClO_4$ were mixed with those containing $Na_2Co^{II}L$ and $NaClO_4$. All the reactions were followed at 540 nm, a λ_{max} for $Co^{III}L^-$, and the pH of the reaction mixtures was between 5 and 6. Observed rate constants which were computed from the first-order and second-order data using the appropriate integrated rate equations are given in Table III.

In order to calculate $-d([I_2]_T)/dt$ from the absorbance in the initial rate measurements, the following values of the molar absorptivity (M^{-1} cm^{-1}) at 540 nm were used:[12,13] 305 for $Co^{III}CyDTA^-$, 324 for $Co^{III}EDTA^-$, 5.4 for $Co^{II}CyDTA^{2-}$ and for $Co^{II}EDTA^{2-}$. The stability constant of I_3^- and therefore the absorbance due to $(I_2)_T$ vary with temperature. At each temperature, the Δ (molar absorptivity) necessary to calculate $d([I_2]_T)/dt$ was obtained from the intercepts of the absorbance curves at zero time. Table IV gives the initial rate data for the $Co^{II}L^{2-}$-iodine reactions. The total iodine and iodide ion concentrations in Table IV refer to the average values over the time of the initial rate measurement.

Table V presents the resolved rate constants for the I_2 and I_3^- oxidations. The k_2 values are the least-squares slopes of the plots shown in Figures 3 (CyDTA) and 4 (EDTA). However, the k_1 values were calculated by correcting the initial-rate k_0 values (given in Table IV) for the k_2 contributions at the existing iodide ion concentrations. More precise values of k_1 can be obtained in this manner than from the intercepts of Figures 3 and 4 because of the predominance of the k_1 path under the initial rate conditions. Nevertheless these intercepts are given with their standard deviations in Table V, to show that the experimental error of the intercept embraces k_1 in all cases.

Discussion

Table VI summarizes the rate constants at 25° and the activation parameters of the reactions under study. For a given $Co^{II}L^{2-}$ complex the k_1 and k_2 values are similar for X_2 and X_3^-, despite the electrostatic repulsion expected for X_3^- and the less favorable free energy change in transferring an electron to X_3^-. A compensating effect is the stronger Lewis basicity of X_3^- compared to X_2. Coordination of X_3^- to cobalt(II) will be more favorable and will tend to offset the more difficult electron-transfer reaction. As a result the $\Delta H_1^\ddagger$ and $\Delta H_2^\ddagger$ values are the same within experimental error. The similarity of the $\Delta S_1^\ddagger$ and $\Delta S_2^\ddagger$ values for the cobalt(II) reactions is in marked contrast to the behavior of

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(12) E. Jacobsen and A. R. Selmer-Olsen, *Anal. Chim. Acta*, **25**, 476 (1961).

(13) M. Mori, M. Shibata, E. Jyono, and H. Nakajima, *Bull. Chem. Soc. Jap.*, **29**, 887 (1956).

Table VI. Rate Constant and Activation Parameter Data for the Oxidation of $Co^{II}L^{2-}$ by X_2 (k_1) and X_3^- (k_2)[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
$Co^{II}CyDTA^{2-}$, 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
$Co^{II}EDTA^{2-}$, I_2, I_3^-	5.2×10^{-4}	23 ± 2	$+1 \pm 6$	3.1×10^{-5}	25 ± 3	$+5 \pm 9$
$Co^{II}CyDTA^{2-}$, Br_2, Br_3^-	2.0×10^{-3}	18.3 ± 0.3	-9.5 ± 0.9	1.1×10^{-3}	18.0 ± 0.3	-12 ± 1
$Co^{II}EDTA^{2-}$, Br_2, Br_3^-	7.3×10^{-2}			5.4×10^{-2}		

[a] Rate constants at 25.0° and $\mu = 1.0$–1.1 *M*.

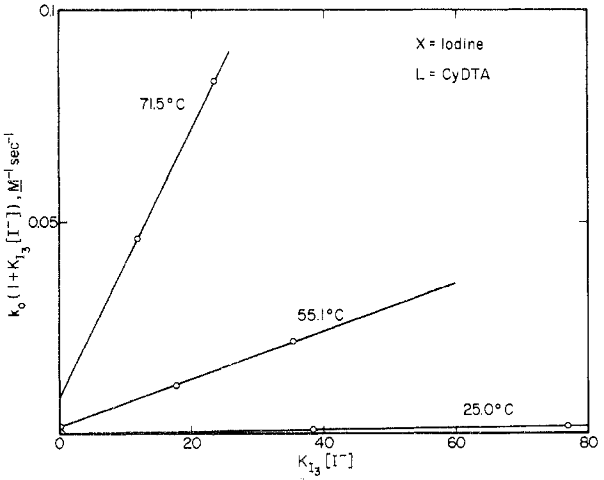

Figure 3. Plot of data used to resolve k_1 (intercept) and k_2 (slope) for the oxidation of $Co^{II}(CyDTA)^{2-}$ by $[I_2]_T$ at the temperatures studied.

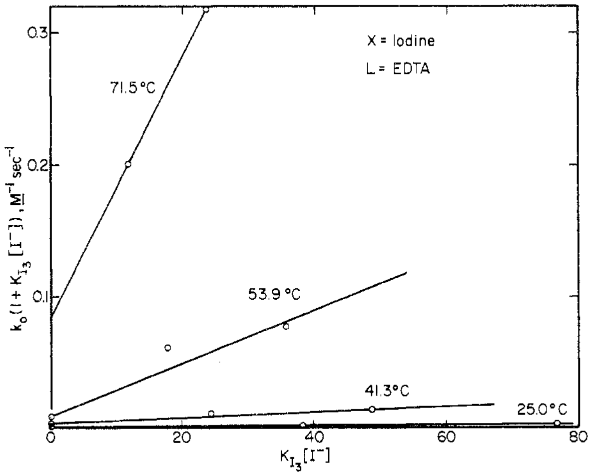

Figure 4. Plot of data used to resolve k_1 (intercept) and k_2 (slope) for the oxidation of $Co^{II}(EDTA)^{2-}$ by $[I_2]_T$ at the temperatures studied.

$Fe^{II}CyDTA^-$ where $\Delta S_1^\ddagger$ is slightly negative while $\Delta S_2^\ddagger$ has a large positive value.[1] The effect of electrostatic repulsion would tend to cause $\Delta S_2^\ddagger$ to be more negative than $\Delta S_1^\ddagger$ by 10-20 eu[14] and although the relatively high ionic strength (∿1 *M*) will moderate the effect, other factors must compensate for the electrostatic repulsion to cause a less extensive reorganizational requirement in attaining the activated complex for X_3^-.

Although $Co^{II}CyDTA^{2-}$ is a slightly better reducing agent than $Co^{II}EDTA^{2-}$, the oxidations of $Co^{II}L^{2-}$ by a particular oxidant are faster, by factors up to 50, when L is EDTA than when L is CyDTA.

The bromine oxidation rates are generally two orders of magnitude faster than the corresponding iodine reactions. Table VI shows that this effect is primarily due to lower $\Delta H^\ddagger$ values in the bromine case. This is expected by analogy to the relative $\Delta H°$ and $\Delta S°$ values between the one-electron reductions of bromine and iodine.[15]

Mechanism of the Oxidation of $Co^{II}L^{2-}$ by Halogens. The reactions under study are inner-sphere oxidations. Direct evidence for the inner-sphere mechanism is available for the oxidation of $Co^{II}L^{2-}$ by bromine, in that the initial product of the oxidation is $[Co^{III}(L)Br]^{2-}$. No $[Co^{III}(L)I]^{2-}$ product is observed in the oxidation of $Co^{II}L^{2-}$ by iodine, but the elimination of I^- from the mixed product is expected to be much faster than the oxidation in this case. This expectation results from the facts that the rate of elimination of X^- from $[Co^{III}(EDTA)X]^{2-}$ is faster for Br^- than for Cl^- [8,9] and the I_2 oxidations are about two orders of magnitude slower than the Br_2 oxidations. Therefore the $[Co^{III}(L)I]^{2-}$ intermediate is not detected. However, the activation parameters suggest that the mechanism of the bromine and iodine oxidations are the same.

The rate of these reactions is determined by a process subsequent to coordination of the oxidant to the metal center; *i.e.*, the reactions are not substitution controlled. This is known because the substitution reactions of $Co^{II}L^{2-}$ are many orders of magnitude faster[16] than the redox reactions in the present study. The process which evidently controls the rate of the oxidation reactions is electron transfer (a term which, as used herein, includes the necessary reorganizations prior to electron transfer). A second candidate for the rate-determining process, atom transfer, can be ruled out on the following basis. The activation energy, if an atom-transfer mechanism were followed, should be related to the homolytic bond energy of the halogen. If this were the case, the iodine oxidations should be faster than those by bromine. The opposite is true, which is consistent with a *bona fide* electron transfer mechanism.

Although it is conceivable that the reactions could proceed *via* two-electron transfer, the facts are not consistent with such a mechanism. The observed yield of $[Co^{III}(EDTA)Br]^{2-}$ from the bromine oxidation of $Co^{II}EDTA^{2-}$ is 100%. The maximum expected yield of this mixed complex, if a cobalt(IV) reaction intermediate is formed, is 50%. Therefore the reactions occur in one-electron steps.

A mechanism consistent with the foregoing discussion is given in eq 5-8, where eq 6 is the rate-determining step (rds).

$$Co^{II}L^{2-} + X_2 \underset{k_d}{\overset{k_f}{\rightleftarrows}} [Co^{II}(L)X_2]^{2-} \quad (5)$$

$$[Co^{II}(L)X_2]^{2-} \xrightarrow[\text{rds}]{k_{ox}} [Co^{III}(L)X]^{2-} + X\cdot \quad (6)$$

$$Co^{II}L^{2-} + X\cdot \xrightarrow{\text{rapid}} [Co^{III}(L)X]^{2-} \quad (7a)$$

(or)

$$X\cdot + X\cdot \xrightarrow{\text{rapid}} X_2 \quad (7b)$$

$$[Co^{III}(L)X]^{2-} \rightarrow Co^{III}L^- + X^- \quad (8)$$

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

(15) W. H. Woodruff and D. W. Margerum, *Inorg. Chem.*, **12**, 962 (1973).

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The mechanism is written for the k_1 path but is equally applicable to the k_2 path (the oxidation by X_3^-). It is impossible to say, on the basis of the results of this study, whether the rapid process after the rate-determining step is oxidation by the halogen radical (eq 7a) or radical recombination (eq 7b). However, halogen radical recombination reactions are known to be extremely fast.[17,18]

Effect of Steric Compression. The resolved rate constants for the oxidations of $Co^{II}L^{2-}$ can be considered to consist of the product of the equilibrium constant for the formation of the intermediate (eq 5) and the rate constant, k_{ox}, for the electron-transfer step (eq 6). Table VII compares the stability constants K and K' for the reaction in eq 9 when L is

$$\mathrm{ML} + \mathrm{B} \underset{k_d}{\overset{k_f}{\rightleftarrows}} \mathrm{M(L)B} \tag{9}$$

EDTA and CyDTA, respectively, for various identities of M and unidentate ligand B. The data presented are selected as representative of a larger body of available information[19] and serve to illustrate the following point. For metals of the approximate size of the first-row transition elements, the stability of M(L)B is one to two orders of magnitude greater for L = EDTA than for L = CyDTA, given a particular M and B. The ratio K/K' appears to be relatively constant despite changes in the charge of M or the magnitude of K.

In CyDTA complexes, there is significant steric interaction between the methylene groups in the 3 and 6 positions of the cyclohexane ring and the methylene groups of two of the glycinate rings of the chelate.[20,21] This effect is known as steric compression and is absent in EDTA complexes. Steric compression has been proposed to be responsible for the increased ring-closure rates of Co^{III}-CyDTA mixed complexes over those of the corresponding EDTA complexes.[22] The decreased stability of mixed complexes, evident in Table VII, when L = CyDTA is probably a manifestation of steric compression in the CyDTA chelates.

The consequence of this ratio of stabilities is the prediction that the rate constant for the oxidation of an EDTA chelate will be one to two orders of magnitude greater than that for the oxidation of a CyDTA chelate if the oxidant occupies a normal coordination position in the inner sphere of the metal ion. As was noted earlier, this prediction is generally upheld for the oxidations of $Co^{II}L^{2-}$ by halogens.

Table VII. Comparison of Stability Constants, K, for Mixed-Complex Formation between ML and B (L = EDTA, CyDTA)

M	B	K, M^{-1} (L = EDTA)	K', M^{-1} (L = CyDTA)	K/K'
Co(II)	CN^-	2×10^3 [a]	39[b]	51
Al(III)[c]	OH^-	1.2×10^8	2.5×10^6	50
Cu(II)	OH^-	251[d]	3.14[e]	80
Fe(III)	O_2H^-	9.8×10^3 [f]	742 [g]	13
Ni(II)[h]	CN^-	1.2×10^4	310	39

[a] S. Nakamura, Ph.D. Thesis, University of Chicago, 1964. [b] Reference 16. [c] G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta,* **37**, 937 (1954). [d] T. R. Bhat and M. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **25**, 1147 (1963). [e] J. D. Carr, Ph.D. Thesis, Purdue University, 1966. [f] M. T. Beck and B. Csiszar, *Magy. Kem. Foly.*, **66**, 259 (1960). [g] M. Orhanovic and R. G. Wilkins, *Croat. Chem. Acta,* **39**, 149 (1967). [h] D. W. Margerum and L. I. Simandi, *Proc. Int. Conf. Coord. Chem.*, **9**, 37 (1966).

Conclusions

The evidence developed here indicates that the oxidations of $Co^{II}L^{2-}$ by halogens proceed *via* an inner-sphere mechanism in which one-electron transfer is the rate-determining step. Steric compression effects are invoked to explain the relative rate behavior of the CyDTA and EDTA complexes. The X_3^- reactions are slower than the X_2 reactions, but the better coordinating ability of X_3^- appears to offset its electrostatic repulsion and less favorable electron-transfer characteristics. Thus, the ratios of k_1/k_2 are not very large and equal 2.9, 16.7, 1.8, and 1.3 for the systems studied. The $\Delta H_1^\ddagger$ and $\Delta H_2^\ddagger$ values for a given system are the same within experimental error. However, the $\Delta H_1^\ddagger$ and $\Delta H_2^\ddagger$ values for bromine are 3 kcal mol^{-1} smaller than those for iodine. The $\Delta S_2^\ddagger$ values for the I_3^- and for the Br_3^- reactions with Co^{II}-CyDTA^{2-} are approximately −10 eu in marked contrast to the large positive $\Delta S_2^\ddagger$ value (+28 eu) for the reaction of I_3^- and Fe^{II}CyDTA^{2-}. The oxidation of Co^{II}CyDTA^{2-} by I_2 is 10 orders of magnitude slower than the oxidation of Fe^{II}CyDTA^{2-} by I_2, a truly striking difference in rate for two so similar reactant pairs.

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Registry No. Co^{II}EDTA^{2-}, 14931-83-0; Co^{II}CyDTA^{2-}, 28161-91-3; I_2, 7553-56-2; I_3^-, 14900-04-0; Br_2, 7726-95-6; Br_3^-, 14522-80-6.

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