$$S = \frac{[\mathrm{NiHL}](\alpha_4 - \alpha_3) + [\mathrm{H^+}]}{[\mathrm{NiHL}]\alpha_4 + [\mathrm{H^+}] + K_\mathrm{M}} \tag{A2}$$

$$\alpha_1 = \left(\frac{[\mathrm{HL^{2+}}]}{[\mathrm{H^+}]} + \frac{[\mathrm{H_2L^-}]}{K_{2a}} + 4\frac{[\mathrm{H_3L}]}{K_{3a}} + 1 + \frac{[\mathrm{In}] + [\mathrm{H^+}] + K_\mathrm{In}}{[\mathrm{H^+}] + K_\mathrm{In}}\right)\Big/ \sigma \tag{A3}$$

$$\sigma = \left(1 + \frac{[\mathrm{In}] + [\mathrm{H^+}] + K_\mathrm{In}}{[\mathrm{H^+}] + K_\mathrm{In}}\right)\left(1 + \frac{K_{1a}}{[\mathrm{H^+}]} + \frac{[\mathrm{H^+}]}{K_{2a}} + \frac{[\mathrm{H^+}]^2}{K_{2a}K_{3a}}\right) + \frac{[\mathrm{HL^{2-}}]}{[\mathrm{H^+}]}\left(1 + 2\frac{[\mathrm{H^+}]}{K_{2a}} + 3\frac{[\mathrm{H^+}]^2}{K_{2a}K_{3a}}\right) + 2\frac{[\mathrm{H_2L^-}]K_{1a}}{K_{2a}[\mathrm{H^+}]} - \frac{[\mathrm{H_2L^-}]}{K_{2a}}\left(\frac{[\mathrm{H^+}]^2}{K_{2a}K_{3a}} - 1\right) + 2\frac{[\mathrm{H_3L}]}{K_{3a}}\left(3\frac{K_{1a}}{[\mathrm{H^+}]} + \frac{[\mathrm{H^+}]}{K_{2a}} + 2\right) \tag{A4}$$

$$\alpha_2 = \left(\frac{[\mathrm{HL^{2-}}]}{[\mathrm{H^+}]} - \frac{[\mathrm{H_2L^-}]}{K_{2a}} - 2\frac{[\mathrm{H_3L}]}{K_{3a}}\right)\Big/ \sigma \tag{A5}$$

$$\alpha_3 = \left(\frac{K_{1a}}{[\mathrm{H^+}]} - \frac{[\mathrm{H^+}]}{K_{2a}} - \frac{[\mathrm{H^+}]^2}{K_{2a}K_{3a}}\right)\Big/ \sigma \tag{A6}$$

$$\alpha_4 = \left(1 + \frac{K_{1a}}{[\mathrm{H^+}]} + \frac{[\mathrm{H^+}]}{K_{2a}} + \frac{[\mathrm{H^+}]^2}{K_{2a}K_{3a}}\right)\Big/ \sigma \tag{A7}$$

If the first term in eq A4 is much greater than the others, it is clear that the expression for α_4 reduces to

$$\frac{1}{1 + \dfrac{[\mathrm{In}] + [\mathrm{H^+}] + K_\mathrm{In}}{[\mathrm{H^+}] + K_\mathrm{In}}}$$

as in eq 2 in the text.

For cobalt, the single relaxation time is calculated analogously from the linear differential rate equation in one variable.

The previously undefined α term is

$$\alpha = \frac{\gamma K_{1a} - \epsilon[\mathrm{HL^{2-}}]}{\gamma[\mathrm{H^+}]} + \frac{\gamma[\mathrm{H^+}] + \epsilon[\mathrm{H_2L^-}]}{\gamma K_{2a}} + \frac{\gamma[\mathrm{H^+}]^2 + 2\epsilon[\mathrm{H^+}][\mathrm{H_2L^-}]}{\gamma K_{2a}K_{3a}} \tag{A8}$$

where

$$\gamma = 1 + \frac{[\mathrm{In}] + [\mathrm{H^+}] + K_\mathrm{In}}{[\mathrm{H^+}] + K_\mathrm{In}} + \frac{[\mathrm{HL^{2-}}]}{[\mathrm{H^+}]} + \frac{[\mathrm{H_2L^-}]}{K_{2a}} + 4\frac{[\mathrm{H_3L}]}{K_{3a}} \tag{A9}$$

$$\epsilon = \frac{K_{1a}}{[\mathrm{H^+}]} - \frac{[\mathrm{H^+}]}{K_{2a}} - 2\frac{[\mathrm{H^+}]^2}{K_{2a}K_{3a}} \tag{A10}$$

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Kinetics and Mechanism of the Oxidation of Cobalt(II) Aminopolycarboxylate Complexes by Hypobromous Acid and Hypobromite Ion

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The oxidation of $[\mathrm{Co^{II}L}]^{2-}$ (L is ethylenediaminetetraacetate, $\mathrm{EDTA^{4-}}$, and *trans*-1,2-diaminocyclohexane-*N,N,N′,N′*-tetraacetate, $\mathrm{CyDTA^{4-}}$) by bromine is studied as a function of pH. As the pH is increased, the identity of the kinetically important oxidant changes from a mixture of $\mathrm{Br_2}$ and $\mathrm{Br_3^-}$ to HOBr and finally to $\mathrm{OBr^-}$. The reactions are first order in $[\mathrm{Co^{II}L}]^{2-}$ concentration and first order in the bromine species. The values of the rate constants (M^{-1} $\mathrm{sec^{-1}}$) for the oxidations by $\mathrm{Br_2}$, HOBr, and $\mathrm{OBr^-}$ when L is EDTA are 7.3×10^{-2}, 65, and 2000, respectively, and when L is CyDTA, the values are 2.0×10^{-3}, 0.16, and 49, respectively. The product of the oxidation of $[\mathrm{Co^{II}L}]^{2-}$ by HOBr and $\mathrm{OBr^-}$ is either $[\mathrm{Co^{III}(L)OH_2}]^-$ or $[\mathrm{Co^{III}(L)OH}]^{2-}$, depending upon pH. Postoxidation ring closure gives $[\mathrm{Co^{III}L}]^{2-}$ where L is six-coordinate. This is a fast process for CyDTA and a rapid scan spectrophotometer is used to observe the oxidation and ring closure steps.

Introduction

The cobalt(II) complexes of EDTA and CyDTA, $[\mathrm{Co^{II}L}]^{2-}$, are oxidized by bromine species in aqueous solution as shown in eq 1. The reactions are first order in $[\mathrm{Co^{II}L}]^{2-}$ concentration and first order in $[\mathrm{Br_2}]_\mathrm{T}$, where $[\mathrm{Br_2}]_\mathrm{T} = [\mathrm{Br_2}] + [\mathrm{Br_3^-}] + [\mathrm{HOBr}] + [\mathrm{OBr^-}]$. The rate constants due to the various bromine species are designated in eq 2-5, and these four rate constants can be evaluated by variation of pH and the bromide ion concentration. The kinetics and mechanism of the oxidation of $[\mathrm{Co^{II}L}]^{2-}$ by $\mathrm{Br_2}$ and $\mathrm{Br_3^-}$ are reported elsewhere.[1] The present paper describes the study of reaction 1 as a function of pH, in order to determine the kinetics and mechanism of the oxidation of $[\mathrm{Co^{II}L}]^{2-}$ by HOBr and $\mathrm{OBr^-}$.

$$2[\mathrm{Co^{II}L}]^{2-} + \left[\begin{array}{c} \mathrm{Br_3^-} \\ \uparrow\downarrow \\ \mathrm{Br_2 + Br^-} \\ \uparrow\downarrow \\ \mathrm{HOBr + 2Br^- + H^+} \\ \uparrow\downarrow \\ \mathrm{OBr^- + 2Br^- + 2H^+} \end{array}\right] \rightarrow 2[\mathrm{Co^{III}L}]^- + 3\mathrm{Br}^- \tag{1}$$

$$[\mathrm{Co^{II}L}]^{2-} + \mathrm{Br_2} \xrightarrow{k_1} \text{products} \tag{2}$$

$$[\mathrm{Co^{II}L}]^{2-} + \mathrm{Br_3^-} \xrightarrow{k_2} \text{products} \tag{3}$$

$$[\mathrm{Co^{II}L}]^{2-} + \mathrm{HOBr} \xrightarrow{k_3} \text{products} \tag{4}$$

$$[\mathrm{Co^{II}L}]^{2-} + \mathrm{OBr^-} \xrightarrow{k_4} \text{products} \tag{5}$$

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(1) W. H. Woodruff, B. A. Burke, and D. W. Margerum, to be submitted for publication.

Hydrolysis of Bromine. The major hydrolytic and protonation equilibria of bromine are given by eq 6-10.

$$Br_2 + H_2O \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} HOBr + H^+ + Br^- \quad K_6 \tag{6}$$

$$2HOBr \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} BrO_2^- + 2H^+ + Br^- \quad K_7 \tag{7}$$

$$HOBr + BrO_2^- \underset{k_{-8}}{\overset{k_8}{\rightleftarrows}} BrO_3^- + H^+ + Br^- \quad K_8 \tag{8}$$

$$3HOBr \rightleftarrows BrO_3^- + 3H^+ + 2Br^- \quad K_9 \tag{9}$$

$$HOBr \rightleftarrows H^+ + OBr^- \quad K_{10} \tag{10}$$

Reaction 6 has been investigated in detail using relaxation techniques,[2] whereby a value of k_6 was determined as 110 sec^{-1} at 20°. Reactions 7 and 8 were too slow to interfere with this relaxation study. The value of K_6 has been determined as 9.6×10^{-9} M^2.[3] Reaction 7 has been reported to be the rate-determining step in the formation of BrO_3^- from Br_2.[4,5] The values of k_7, k_{-7}, and k_8 at 25° were reported to be 8×10^{-4} M^{-1} sec^{-1}, 1.5×10^{-4} M^{-3} sec^{-1}, and 0.018 M^{-1} sec^{-1}, respectively. The value of the equilibrium constant K_9 is 8×10^{-12} M^3 [6] and of the dissociation constant K_{10} is 2.4×10^{-9} M.[7]

The primary points concerning hydrolysis are that the Br_2-HOBr equilibrium is rapid compared to the oxidation reactions of $[Co^{II}L]^{2-}$ and that reaction 7 is slow compared to the time scale of the experiments in the present study. Therefore hydrolysis beyond HOBr can be neglected.

Experimental Section

The experiments described were performed in the presence of excess bromide ion, $[Br^-]_T = 0.100$ M. This allows a comparison of the k_0 (k_0 is the second-order rate constant as defined in eq 11) values obtained, by fixing the Br_2:Br_3^- ratio and varying the Br_2:HOBr:OBr^- ratio by changing the pH. Br^- concentrations other than 0.1 M were tested to verify the expected Br^- dependence of k_0. Experimental rate constants were determined under pseudo-first-order conditions testing with one reactant and then the other in excess.

$$-d([Br_2]_T)/dt = k_0[Br_2]_T[[Co^{II}L]^{2-}] \tag{11}$$

Kinetics measurements were made, depending upon the speed of a given reaction, using either a Durrum stopped-flow spectrophotometer (cell path 2.0 cm) or a Cary 16 spectrophotometer interfaced to a Varian G-2000 recorder. The stopped-flow instrument was interfaced to a Hewlett-Packard 2115A general-purpose computer (8K × 16 bit memory) as described elsewhere.[1,8] The reactions were followed at 540 nm, where the molar absorptivities (M^{-1} cm^{-1}) are 324 for $[Co^{III}EDTA]^-$, 305 for $[Co^{III}CyDTA]^-$, and 5.4 for both $[Co^{II}EDTA]^{2-}$ and $[Co^{II}CyDTA]^{2-}$.

Routine spectra were taken using a Cary 14 spectrophotometer. The temperature was maintained at 25.0 ± 0.1° for all studies. Buffer concentrations were 0.10 M for all experiments, the identity of the buffer being either acetate, phosphate, or borate depending upon the pH desired. All experiments were carried out in the presence of 1.00 M $NaClO_4$, which was recrystallized twice before use. The different buffers used at the various pH values studied and the degree of protonation of these buffers lead to slight differences in ionic strength among the experiments. The effect of these differences in ionic strength was assumed to be negligible.

Bromine stock solutions were prepared by dissolving liquid bromine in an aqueous solution of 1 M NaBr and 10^{-3} M $HClO_4$. The total bromine concentration was approximately 0.1 M. Immediately prior to use the stock solutions were standardized spectrophotometrically at the isosbestic point of Br_2 and Br_3^- (λ 457 nm, ε 98 M^{-1} cm^{-1}). Bromine solutions for an individual experiment were prepared by adding the required volume of the stock solution to the appropriate buffer immediately prior to the experiment. Standard solutions of $[Co^{II}L]^{2-}$ were prepared by direct weighing of $Na_2Co^{II}CyDTA \cdot 3H_2O$ and $Na_2Co^{II}EDTA \cdot 2H_2O$, which were isolated by the method of Schwarzenbach and Parissakis.[9] Measurements of pH were made using an Instrumentation Laboratories Model 245 meter and a reference electrode containing saturated NaCl.

Methods of Product Identification. The initial products of the oxidation reactions are mixed complexes having the general formula $[Co^{III}(L)B]^{n-}$, where B is either Br^-, H_2O, or OH^- depending upon the identity of the oxidant and the pH. The mixed product undergoes ring closure with varying rapidity, depending upon the identity of L and B, giving $[Co^{III}L]^-$ as a final product. In the cases where the ring closure reaction was sufficiently slow, it was possible to identify $[Co^{III}LB]^{n-}$ using spectra taken in a conventional manner. In other cases, it was necessary to use special techniques to obtain the spectra of the initial products. One such technique is to reconstruct the spectrum using the stopped-flow instrument to observe the oxidation at a number of properly spaced wavelengths. This method is applicable when the oxidation reaction is substantially faster than the ring closure.

A much more convenient technique for the identification of $[Co^{III}(L)B]^{n-}$ is the use of a swept electron beam rapid-scan spectrophotometer, such as has been described recently.[10] This method offers the advantage of giving a series of continuous spectra taken at a specified time interval of a single reaction mixture, rather than simply the spectrum at the completion of the oxidation reaction. Thus the rapid-scan technique can identify $[Co^{III}(L)B]^{n-}$, even when the oxidation and ring closure rates are not well separated.

The instrument used for the rapid-scan experiments was similar to that described previously,[10] but in a refined form. A stopped-flow cell with a 3-mm light path, having the same design as reported previously,[8] was fitted to the spectrophotometer. The spectra were scanned using a Tektronix J20 Prototype spectrometer probe, which employs a Vidicon tube as a detector. The spectrometer probe is capable of recording a 400-nm spectral scan in a minimum of 4 msec. The detector was interfaced to a Digital Equipment Corp. PDP-12 general-purpose computer (8K × 12 bit memory). The computer records spectra at preselected time intervals, transforms the signals to transmittance, and displays the final data on a storage oscilloscope. Using this system it was possible to obtain and store eight spectral scans per experiment. The duration of each scan was 20 msec, and the scan repetition rate could be varied from 20 msec to as long an interval as desired. The spectral range scanned could be selected as 40 or 400 nm, beginning at various wavelengths in the visible region. The spectra obtained could be displayed individually or could be superimposed upon one another. A didymium glass was used to calibrate the wavelength of the spectrometer.

Results and Discussion

At pH values near 3.5 and in the presence of at least 0.1 M bromide ion, Br_2 and Br_3^- are the only kinetically important oxidants in reaction 1. The product of the oxidation under these conditions is $[Co^{III}(L)Br]^{2-}$. As the pH is increased, k_0 increases smoothly for the oxidations of both $[Co^{II}L]^{2-}$ complexes until a constant value of k_0 with pH is reached. This occurs at pH 8 for the CyDTA complex and above pH 9 for the EDTA complex. The increase in k_0 with pH is due to the increasing fraction of $[Br_2]_T$ which is represented by HOBr and OBr^- and to the greater rate of the oxidation reaction with these species. The kinetics data for the pH dependence of k_0 are given in Table I for $[Co^{II}EDTA]^{2-}$ and in Table II for $[Co^{II}CyDTA]^{2-}$. The values of k_{app} were determined under pseudo-first-order conditions, where k_{app} is defined as shown in eq 12, R being the reagent not in excess.

$$-\frac{d[R]}{dt} = k_{app}[R] \tag{12}$$

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(2) M. Eigen and K. Kustin, *J. Amer. Chem. Soc.*, **84**, 1355 (1962).

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(4) P. Engel, A. Oplatka, and B. Perlmutter-Hayman, *J. Amer. Chem. Soc.*, 76, 2010 (1954).

(5) B. Perlmutter-Hayman and G. Stein, *J. Phys. Chem.*, 63, 734 (1959).

(6) P. J. M. Radford in "Bromine and Its Compounds," Z. E. Jolles, Ed., Academic Press, New York, N. Y., 1966, p 154.

(7) M. Anbar and H. Taube, *J. Amer. Chem. Soc.*, **80**, 1073 (1958).

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

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

(10) R. E. Santini, M. J. Milano, H. L. Pardue, and D. W. Margerum, *Anal. Chem.*, **44**, 826 (1972).

Table I. Kinetics of the Oxidation of $[\mathrm{Co^{II}EDTA}]^{2-}$ by Bromine at Various pH Values[a]

pH	$[\mathrm{Br_2}]_T$, *M*	$[[\mathrm{Co^{II}EDTA}]^{2-}]$, *M*	k_{app}, $\mathrm{sec^{-1}}$	k_0 $M^{-1}\ \mathrm{sec^{-1}}$
3.5[b]	Variable	Variable		0.059[c]
5.34[b]	1×10^{-3}	0.100	0.059 ± 0.003	0.59
6.58[d]	8.5×10^{-3}	1.00×10^{-3}	0.148 ± 0.002	8.7
8.26[e]	8.5×10^{-3}	1.00×10^{-3}	11.5 ± 0.3	675
8.95[e]	8.5×10^{-3}	1.00×10^{-3}	23.1 ± 0.3	1360
9.26[e]	8.5×10^{-3}	1.00×10^{-3}	26.6 ± 0.2	1570

[a] At 25.0°, $[\mathrm{Br^-}]_T = 0.100\ M$, $[\mathrm{NaClO_4}] = 1.0\ M$, $[\mathrm{buffer}]_T = 0.1\ M$, λ 540 nm. [b] Acetate buffer. [c] Reference 1. [d] Phosphate buffer. [e] Borate buffer.

Table II. Kinetics of the Oxidation of $[\mathrm{Co^{II}CyDTA}]^{2-}$ by Bromine at Various pH Values[a]

pH	$[\mathrm{Br_2}]_T$, *M*	$[[\mathrm{Co^{II}CyDTA}]^{2-}]$, *M*	k_{app}, $\mathrm{sec^{-1}}$	k_0, M^{-1} $\mathrm{sec^{-1}}$
3.5[b]	Variable	Variable		0.0015[c]
5.03[b]	8.5×10^{-3}	1.00×10^{-3}	3.72×10^{-5}	0.0022
6.59[d]	8.5×10^{-3}	1.00×10^{-3}	1.29×10^{-3}	0.076
7.98[e]	5×10^{-4}	0.0500	0.41 ± 0.01	8.2
8.00[e]	2×10^{-4}	0.0250	0.208 ± 0.006	8.3
8.00[e]	1×10^{-4}	0.0250	0.170 ± 0.007	6.8
8.00[e]	2×10^{-4}	0.125	0.090 ± 0.005	7.2
8.00[e]	1×10^{-4}	0.125	0.086 ± 0.004	6.9
8.27[e]	8.5×10^{-3}	1.00×10^{-3}	0.145 ± 0.008	8.5
8.95[e]	8.5×10^{-3}	1.00×10^{-3}	0.154 ± 0.003	9.1
9.25[e]	8.5×10^{-3}	1.00×10^{-3}	0.156 ± 0.001	9.2

[a] At 25.0°, $[\mathrm{Br^-}]_T = 0.100\ M$, $[\mathrm{NaClO_4}] = 1.0\ M$, $[\mathrm{buffer}]_T = 0.1\ M$, λ 540 nm. [b] Acetate buffer. [c] Reference 1. [d] Phosphate buffer. [e] Borate buffer.

Therefore, due to the 2:1 stoichiometry of the reactions and the convention chosen of expressing k_0 in terms of $-\mathrm{d}[\mathrm{Br_2}]_T/\mathrm{d}t$, k_0 was calculated from k_{app} in the following manner: $k_0 = k_{app}/2[\mathrm{Br_2}]_T$ for the experiments in which R is $[\mathrm{Co^{II}L}]^{2-}$, and $k_0 = k_{app}/[[\mathrm{Co^{II}L}]^{2-}]$ when [R] is $[\mathrm{Br_2}]_T$.

Resolution of the Rate Constants Due to Hypobromous Acid and Hypobromite Ion. Figure 1 shows the distribution of bromine species as a function of pH, in the presence of 0.1 *M* bromide ion. Comparison of the data in Tables I and II with Figure 1 shows that, although bromine is less than 5% hydrolyzed at pH 6, the hydrolyzed species are already the kinetically important reactants.

The expression for k_0 is given by eq 13, where $f_{\mathrm{oxidant}} = [\mathrm{oxidant}]/[\mathrm{Br_2}]_T$.

$$k_0 = k_1 f_{\mathrm{Br_2}} + k_2 f_{\mathrm{Br_3^-}} + k_3 f_{\mathrm{HOBr}} + k_4 f_{\mathrm{OBr^-}} \qquad (13)$$

The values of k_1 and k_2 were determined[1] below pH 4 and the values of k_3 and k_4 were determined by weighted multiple linear regression upon eq 13 and the k_0 data in either Table I or II. For reasons which will be discussed, the data for $[\mathrm{Co^{II}CyDTA}]^{2-}$ above pH 8 were omitted from this calculation. The resolved rate constant with their average deviations are given in Table III. Using these rate constants, a calculated pH profile for the oxidation of $[\mathrm{Co^{II}L}]^{2-}$ by bromine can be constructed. Figure 2 shows the calculated curves for $[\mathrm{Co^{II}EDTA}]^{2-}$ and $[\mathrm{Co^{II}CyDTA}]^{2-}$, together with the experimental points for the two complexes. The faster oxidation of the EDTA complex compared to the CyDTA complex is attributable to the more stable Co(II)-oxidant inner-sphere intermediate in the former case.[1] The inner-sphere hypothesis is confirmed in part by identification of the products of these reactions and by the relative rate constants.

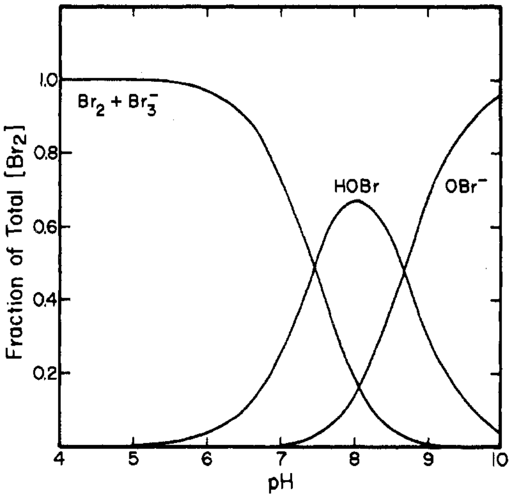


Figure 1. Species distribution of bromine, hypobromous acid, and hypobromite ion in 0.1 *M* bromide ion as a function of pH; $K_{\mathrm{Br_3^-}} = 16.9\ M^{-1}$, $K_6 = 9.6 \times 10^{-9}\ M^2$, $K_{10} = 2.4 \times 10^{-9}\ M$.

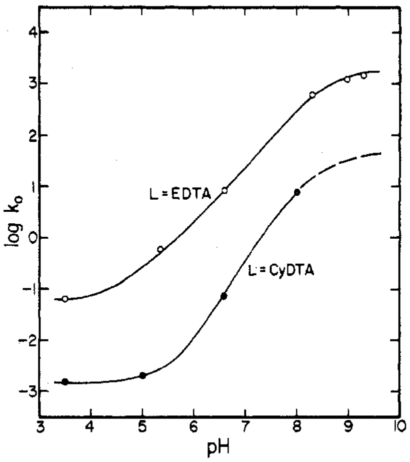


Figure 2. The log k_0-pH profile of the composite second-order rate constant for the oxidation of $[\mathrm{Co^{II}L}]^{2-}$ by $[\mathrm{Br_2}]_T$. The points are experimental and the lines are calculated from the rate constants in Table III. The dashed section of the calculated line for CyDTA indicates the region for which the experimental k_0 values are not reliable due to interference from postoxidation ring closure.

Table III. Resolved Rate Constants for the Oxidation of $[\mathrm{Co^{II}L}]^{2-}$ by $\mathrm{Br_2}$, $\mathrm{Br_3^-}$, HOBr, and $\mathrm{OBr^-}$ (25.0°, $\mu = 1.1\text{-}1.2\ M$ (1.0 *M* $\mathrm{NaClO_4}$))

Oxidizing agent	Rate const	Value, M^{-1} $\mathrm{sec^{-1}}$, with av dev for	
		$[\mathrm{Co^{II}EDTA}]^{2-}$	$[\mathrm{Co^{II}CyDTA}]^{2-}$
$\mathrm{Br_2}$	k_1[a]	$(7.3 \pm 0.8) \times 10^{-2}$	$(2.0 \pm 0.4) \times 10^{-3}$
$\mathrm{Br_3^-}$	k_2[a]	$(5.42 \pm 0.07) \times 10^{-2}$	$(1.11 \pm 0.05) \times 10^{-3}$
HOBr	k_3	65 ± 5	0.16 ± 0.01
$\mathrm{OBr^-}$	k_4	2000 ± 140	49 ± 3

[a] Reference 1.

Identification of Products. Table IV gives the absorbance maxima (between 500 and 600 nm) and molar absorptivity values for some possible products of the reactions under study. The differences in the absorption spectra among these complexes provided the primary means of identification of the products of the oxidation reactions.

The initial product of the oxidation of $[\mathrm{Co^{II}L}]^{2-}$ by $\mathrm{Br_2}$ and $\mathrm{Br_3^-}$ is $[\mathrm{Co^{III}(L)Br}]^{2-}$.[1] This mixed complex then eliminates bromide ion to form ring-closed $[\mathrm{Co^{III}L}]^-$. No detectable amount of $[\mathrm{Co^{III}(L)Br}]^{2-}$ is produced when the oxidant is HOBr or $\mathrm{OBr^-}$.

Above pH 6 $\mathrm{Br_2}$ and $\mathrm{Br_3^-}$ are no longer important reactants and the initial product of the oxidation reaction is either $[\mathrm{Co^{III}(L)OH_2}]^-$ or $[\mathrm{Co^{III}(L)OH}]^{2-}$, depending on the pH. These species can be detected by the rapid-scan method described in the Experimental Section. Conditions for these

Table IV. Absorbance Maxima and Molar Absorptivities of Cobalt(III) Complexes

Complex	λ_{max}, nm [ϵ, M^{-1} cm^{-1}] L = EDTA	λ_{max}, nm [ϵ, M^{-1} cm^{-1}] L = CyDTA
$[Co^{III}L]^-$	538 [338][a]	540 [305][c]
$[Co^{III}(L)OH_2]^-$	550 [270][a]	550 [300][d]
$[Co^{III}(L)OH]^{2-}$	570 [215][a]	(570 [230])[e]
$[Co^{III}(L)Br]^{2-}$ ("isomeric")	590 [234][b]	(590 [260])[e]

[a] I. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 260 (1958). [b] M. Mori, M. Shibati, E. Joyno, and H. Nakajima, *Bull. Chem. Soc. Jap.*, 29, 887 (1956). [c] E. Jacobsen and A. R. Selmer-Olsen, *Anal. Chem. Acta*, 25, 476 (1961). [d] R. E. Yelin, Ph.D. Thesis, State University of New York at Buffalo, 1969. [e] Estimated by comparison to $[Co^{III}(L)Cl]^{2-}$ spectra: B. Grossman, Ph.D. Thesis, State University of New York at Buffalo, 1969.

experiments were the same as given in Tables I and II, except that the original concentration of $[Co^{II}L]^{2-}$ was 3×10^{-3} M. In the case of the CyDTA complex, both the formation and ring closure of $[Co^{III}(CyDTA)OH]^{2-}$ can be observed using the rapid-scan technique, by observing the shift of the absorption maximum of the product from 570 to 540 nm. The formation of the hydroxo intermediate is seen in eight spectral scans taken 1 sec apart. Both the oxidation and ring closure reactions are seen when the scan repetition rate is 5 sec. In the case of the oxidation of $[Co^{II}EDTA]^{2-}$ at pH >8, the hydroxo product was confirmed by reconstruction of the spectrum from data taken at ten wavelengths between 500 and 620 nm, using the Durrum stopped-flow instrument. This was possible because the oxidation reaction is much faster than the ring closure reaction for the EDTA complexes.

Reaction 14 has a pK_a value of approximately 8[11] and the equilibrium should be established very rapidly. The products

$$[Co^{III}(EDTA)OH_2]^- \rightleftarrows [Co^{III}(EDTA)OH]^{2-} + H^+ \qquad (14)$$

of the oxidation reaction below and above pH 8 are rapidly interconvertible, as shown by their visible spectra, providing further proof that the products are the aquo and hydroxo mixed complexes.

Postoxidation Ring Closure Reactions. The term ring closure refers to the reaction in eq 15, where the reactant

$$[Co^{III}(L)B]^{n-} \xrightarrow{k_{rc}} [Co^{III}L]^- + B^{(n-1)-} \qquad (15)$$

contains five-coordinate L and the foreign ligand B (B is Br^-, H_2O, or OH^-) and L becomes six-coordinate in the product.

Under the conditions of the present study, reaction 15 is substantially slower for $[Co^{III}(EDTA)B]^{n-}$ than the oxidation of $[Co^{II}EDTA]^{2-}$ by total Br_2. Therefore reliable kinetics data can be gathered for the oxidation reaction in this system without interference from the k_{rc} step. When L is CyDTA, on the other hand, reaction 15 is much faster than the oxidation reaction at the lower pH values (pH <8). At pH 8 and above, however, the magnitude of the first-order rate constant for the oxidation, k_{app}, is comparable to that of k_{rc}, and the values for the second-order rate constant, k_0, calculated from these k_{app} data are unreliable.

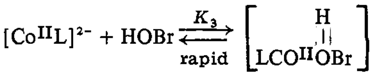
By coincidence this source of error is avoided for the data taken at pH 8. The initial product at this pH is mostly $[Co^{III}(CyDTA)OH_2]^-$ which has a molar absorptivity quite similar to that of $[Co^{III}CyDTA]^-$ at 540 nm.[12] Therefore reaction 15 has little effect upon the value of k_{app} measured at this pH.

Above pH 8 for the CyDTA reaction the absorbance change, from which k_{app} is measured, increases with increasing pH. This behavior is consistent with the expected absorbance changes if the observed reaction is increasingly due to eq 16.

$$[Co^{III}(CyDTA)OH]^{2-} \rightarrow [Co^{III}CyDTA]^- + OH^- \qquad (16)$$

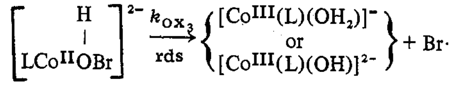
If k_{app} were primarily due to the oxidation of $[Co^{II}CyDTA]^{2-}$, the absorbance change would be expected to decrease above pH 8. Furthermore, the value of k_{app} becomes constant (with pH) at 0.15-0.16 sec^{-1} and is assigned as the constant for reaction 16. Therefore the ring closure of $[Co^{III}(CyDTA)OH]^{2-}$ is 10^4 times faster than that of $[Co^{III}(EDTA)OH]^{2-}$.[11] This compares to a ratio of 5000 for the relative ring closure rates of $[Co^{III}(CyDTA)Cl]^{2-}$ and $[Co^{III}(EDTA)Cl]^{2-}$.[13,14] Steric interactions due to the cyclohexane ring in CyDTA appear to speed its elimination and ring closure reactions compared to the EDTA complexes.

Proposed Mechanism. There is direct evidence that the oxidation reactions with Br_2 and Br_3^- take place by an inner-sphere mechanism because $[Co^{III}LBr]^{2-}$ species are formed before the Br^- ion is eliminated in the ring closure reaction. The greater reactivity of HOBr and the fact that OBr^- is much faster than HOBr, despite its electrostatic repulsion by $[Co^{II}L]^{2-}$, indicate that these species also proceed by inner-sphere coordination to cobalt(II) prior to the electron-transfer step. The initial reaction products and subsequent ring closure reactions, as in the Br_2 and Br_3^- oxidations, provide direct evidence for this pathway. The mechanism proposed in eq 17-23 accounts for the results described. Reactions 19 and 20 are the rate-determining steps (rds). This mechanism is similar to that which is proposed for the oxidations of $[M^{II}L]^{2-}$ by halogens.[1] That no significant fraction of the inner-sphere oxidation takes place with the bromine end of the oxidant bound to the metal ion is demonstrated by the apparent absence of $[Co^{III}(L)Br]^{2-}$ product. Binding *via* the oxygen atom is expected considering the relative basicity of the two ends of the hypobromite moiety.



$$[Co^{II}L]^{2-} + HOBr \underset{rapid}{\overset{K_3}{\rightleftarrows}} \left[\begin{array}{c} H \\ | \\ LCo^{II}OBr \end{array}\right]^{2-} \qquad (17)$$

$$[Co^{II}L]^{2-} + OBr^- \underset{rapid}{\overset{K_4}{\rightleftarrows}} [LCo^{II}OBr]^{3-} \qquad (18)$$



$$\left[\begin{array}{c} H \\ | \\ LCo^{II}OBr \end{array}\right]^{2-} \xrightarrow[rds]{k_{ox_3}} \left\{\begin{array}{c} [Co^{III}(L)(OH_2)]^- \\ or \\ [Co^{III}(L)(OH)]^{2-} \end{array}\right\} + Br\cdot \qquad (19)$$

$$[LCo^{II}OBr]^{3-} \xrightarrow[rds]{k_{ox_4}} \left\{\begin{array}{c} [Co^{III}(L)(OH_2)]^- \\ or \\ [Co^{III}(L)(OH)]^{2-} \end{array}\right\} + Br\cdot \qquad (20)$$

$$2Br \xrightarrow{rapid} Br_2 \qquad (21)$$

$$H_2O + Br_2 \overset{rapid}{\rightleftarrows} \left\{\begin{array}{c} HOBr + H^+ + Br^- \\ or \\ OBr^- + 2H^+ + Br^- \end{array}\right\} \qquad (22)$$

$$\left.\begin{array}{c} [Co^{III}(L)(OH_2)]^- \\ or \\ [Co^{III}(L)(OH)]^{2-} \end{array}\right\} \xrightarrow{k_{rc}} [Co^{III}L]^- + \left\{\begin{array}{c} H_2O \\ or \\ OH^- \end{array}\right\} \qquad (23)$$

The absence of $[Co^{III}(L)Br]^{2-}$ as a product above pH 6 also indicates that the halogen radicals proposed in eq 19 and 20 (which may be Br· as shown or Br_2^-) do not oxidize $[Co^{III}L]^{2-}$ directly but instead recombine and rehydrolyze

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rapidly as shown in eq 21 and 22. The ring closure reactions (eq 23) are quite fast for cobalt(III) complexes but are in accord with other examples of this type.[13,14]

It is often the case that hypohalous acids oxidize a particular substrate faster than the oxidation by the corresponding halogen.[15-18] This effect is seen in the present study, where k_3/k_1 is 80 for $[\mathrm{Co^{II}CyDTA}]^{2-}$ and 890 for $[\mathrm{Co^{II}EDTA}]^{2-}$. Contrary to the prediction which is made on the basis of electrostatics, hypobromite ion oxidizes $[\mathrm{Co^{II}L}]^{2-}$ faster than hypobromous acid. The ratio k_4/k_3 is 310 for the CyDTA complex and 31 for EDTA. This effect is probably due to the increased magnitude of K_4 over K_3 (eq 17 and 18). Hypobromite ion is almost as strong a Bronsted base as $\mathrm{CN^-}$ or $\mathrm{NH_3}$, and this can be expected to be reflected in Lewis basicity as well. Thus, the increased coordinating strength of $\mathrm{OBr^-}$ over HOBr overcomes the electrostatic disadvantage in forming the inner-sphere intermediate with $[\mathrm{Co^{II}L}]^{2-}$.

The ratios of the rate constants for a given oxidant with the EDTA compared to the CyDTA complexes are 37, 49, and 41 for the reactions with $\mathrm{Br_2}$, $\mathrm{Br_3^-}$, and $\mathrm{OBr^-}$, respectively, but the same ratio is 410 for the HOBr reaction. A ratio of approximately 50 is typical for the relative stabilities of monodentate ligands with metal-EDTA compared to metal-CyDTA complexes,[1] so that the behavior of $\mathrm{Br_2}$, $\mathrm{Br_3^-}$, and $\mathrm{OBr^-}$ is consistent with the proposed inner-sphere mechanism. The larger ratio for HOBr suggests that an additional factor such as a more favorable hydrogen-bonding interaction between the coordinating HOBr and an acetate segment of the EDTA enhances the rate relative to the CyDTA complex.

In conclusion, hypobromite ion reacts faster than molecular bromine with $[\mathrm{Co^{II}L}]^{2-}$ by factors of 2.4×10^4 to 2.6×10^4 and the relative rate constants and products are consistent with a mechanism in which the oxidation step is subsequent to coordination of the bromine or hypobromite moiety to the cobalt(II) complex.

Registry No. $[\mathrm{Co^{II}EDTA}]^{2-}$, 14931-83-0; $\mathrm{Br_2}$, 7726-95-6; $[\mathrm{Co^{II}CyDTA}]^{2-}$, 28161-91-3; $\mathrm{Br_3^-}$, 14522-80-6; HOBr, 13517-11-8; $\mathrm{OBr^-}$, 14380-62-2.

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Kinetic Trans Effect Exhibited in the Methanol Exchange of the $\mathrm{Co(CH_3OH)_5py^{2+}}$ Complex

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Nuclear magnetic relaxation times, T_2, were determined as a function of temperature from the line shape analysis of methyl pnmr resonances of the methanol coordinated cis and trans to the pyridine in $\mathrm{Co(CH_3OH)_5py^{2+}}$. From the T_2 data the first-order solvent-exchange rate constants were determined for the cis and trans sites. T_2 and shifts of the bulk solvent methyl resonances were measured and compared to the coordinated solvent nmr data. From this it was concluded that no internal rearrangement was taking place during exchange. This system was found to exhibit a clear-cut example of the kinetic trans effect for a labile octahedral complex in that the trans site exchange rate constant per coordinated methanol molecule was 2.5–3.0 times that for the cis site. The rate constants at $-30°$ are 410 and 1200 $\mathrm{sec^{-1}}$ for the cis and trans sites, respectively. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are respectively 11.9 kcal $\mathrm{mol^{-1}}$ and 2.9 eu for the cis site and 11.2 kcal $\mathrm{mol^{-1}}$ and 2.2 eu for the trans site.

Introduction

Mechanistic inferences[1-3] concerning substitution reactions of the first-row transition metal ions are usually based on rate data for direct substitution reactions and a knowledge of the solvent-exchange rates of most of the fully solvated first-row transition metal ions. Unfortunately, the continued development and extension of our understanding of this type of reaction to substituted divalent metal ions has reached somewhat of an impasse for lack of the appropriate experimental solvent-exchange rate data. In an attempt to circumvent this impasse for at least one chemical system and thereby to establish a model system, efforts in this laboratory have been directed toward measuring the methanol-exchange rate of cobalt(II) complexes.[4,5] The reasons for choosing this system have been discussed in a previous publication.[4]

This paper reports the methanol-exchange rate data for the methanols cis and trans to pyridine (py) in $\mathrm{Co(CH_3OH)_5py^{2+}}$. Pyridine was chosen for this study because of the rather extensive evidence that it possesses π-acceptor properties when coordinated to $\mathrm{Co^{2+}}$.[6] The first exploratory steps in determining what effect a π-acceptor ligand has on the methanol-exchange rates of octahedral cobalt(II) complexes are reported here. Proton nmr was used to measure the line width of both the coordinated and bulk methanol methyl resonances as a function of temperature.

Experimental Section

Sample Preparation. An anhydrous methanol solution of cobaltous perchlorate was prepared by adding cobaltous perchlorate

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