$H^+ + {}^-O_3S\text{-}SO_3^- \rightarrow SO_2 + HSO_4^-$

We report here our observation that the same reaction takes place smoothly at room temperature in 7-10 M sulfuric acid.

Table I

$[H_2SO_4]$, M	Pseudo-first-order rate constant × 10^4, sec^{-1}	$[H_2SO_4]$, M	Pseudo-first-order rate constant × 10^4, sec^{-1}
7.15	0.418	9.28	8.26
7.78	0.820	9.73	19.4
8.30	1.72	10.18	32.0
8.81	4.00	10.52	65.5

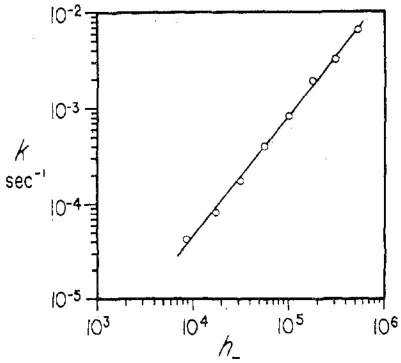

Figure 1. Dependence of the rate on acidity.

Experimental Section

$Na_2S_2O_6 \cdot 2H_2O$ was synthesized by the literature method.[2] Sulfuric acid solutions were made up by mixing appropriate portions of 7 M with 11 M reagent grade H_2SO_4, in each case checked by titration. Each sulfuric acid solution was precooled slightly before adding the dithionate stock solution, so that all final solutions were at 23 ± 1°. The final concentration of dithionate was approximately 0.003 M. The reaction was followed with a Cary 14 spectrophotometer, using the SO_2 absorption at 2790 Å. All rates were first order with respect to dithionate for at least 4 half-lives. The pseudo-first-order rate constant, evaluated graphically, is probably reliable to within about ±2%.

Results and Discussion

The pseudo-first-order rate constant, k, has the values given in Table I, at the stated acid concentration. The dependence of k on the indicator acidity, h_-,[3] is shown in Figure 1. The indicator acidity h_- is reasonable to use, since the protonation of one end of a dithionate ion probably affects the hydration of the other end only slightly. In any event, the indicator acidity function H_{2-} has not been tabulated for these acidic solutions. The slope of the line in Figure 1 is 1.26. The discrepancy between the observed slope and unity is probably without mechanistic significance,[5] indicating merely a slight difference between the hydration of the transition state and of the indicators used to establish the H_- scale. We conclude that the transition state is singly protonated from dilute solutions[1] to the highest acidity reached in this study. We note in passing that the data in Figure 1 show no tendency to level off at high acidities, indicating that dithionic acid is a completely strong diprotic acid up to the highest acidity reached.

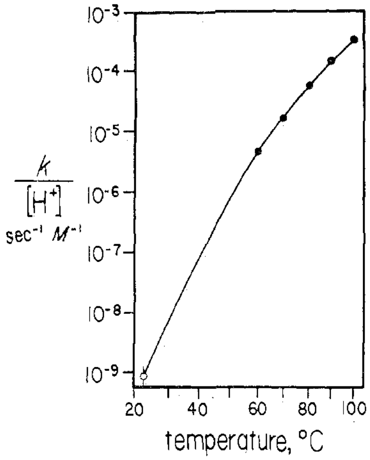

Figure 2. Arrhenius plot of the second-order rate.

In order to compare our second-order rate constant with the literature values at high temperatures, we had to extrapolate our data to infinite dilution. There is no generally accepted way to make this extrapolation. In 1961, Bunnett[4] recommended a log-log plot of k/h vs. water activity, extrapolated to unity water activity. By 1966 he had changed his mind, he and Olsen[5] recommending a log-log plot of k/h vs. $h/[H^+]$, extrapolated to unity value of the latter. We have applied both methods to our data, obtaining good straight lines with both

$$k/h_- = 10^{-8.92}(a_{H_2O})^{-1.0} \text{ sec}^{-1}\ M^{-1}$$

$$k/h_- = 10^{-9.22}(h_-/[H^+])^{+0.27} \text{ sec}^{-1}\ M^{-1}$$

We take the extrapolated value at 23° to be $10^{-9.07\pm0.15}$ sec^{-1} M^{-1}. Figure 2 is an Arrhenius plot of our data with those of Meyer,[1d] which seem to be the best, also extrapolated slightly to infinite dilution. As was already pointed out[1c,d] the Arrhenius plot is curved, but our data are quite compatible with the earlier data. The slope of the curve at 25° corresponds to $\Delta H^\ddagger = 52$ kcal and $\Delta S^\ddagger = +74$ cal deg^{-1}.

Registry No. $Na_2S_2O_6 \cdot 2H_2O$, 10101-85-6.

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[1] (a) M. J. A. Muller, *Bull. Soc. Chim. Fr.*, 9, 183 (1911); (b) D. M. Yost and R. Pomeroy, *J. Amer. Chem. Soc.*, 49, 703 (1927); (c) F. Ishikawa and H. Hagisawa, *Sci. Rep. Tohoku Imp. Univ., Ser. 1*, 21, 484 (1932); (d) J. Meyer, *Z. Anorg. Allg. Chem.*, 222, 337 (1935).

[2] G. Brauer, "Handbook of Preparative Inorganic Chemistry," 2nd ed, Academic Press, New York, N. Y., 1963, p 395.

[3] R. H. Boyd, *J. Amer. Chem. Soc.*, 83, 4288 (1961).

[4] J. F. Bunnett, *J. Amer. Chem. Soc.*, 83, 4956, 4968, 4973, 4978 (1961).

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

Electrophilic Acceleration by Bromine of the Elimination of Bromide Ion from $[Co^{III}(EDTA)Br]^{2-}$

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The ring-closure reactions of mixed halide-aminopolycarboxylate complexes of cobalt(III) have been studied by several workers.[1-5] It has been found that a number of

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[1] M. L. Morris and D. H. Busch, *J. Phys. Chem.*, 63, 340 (1959).

[2] R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, 1998 (1960).

[3] R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, 2788 (1963).

metal ions accelerate this ring closure and that the degree of the acceleration is related to the stability of the acetate and halide complexes of the metal ions.[2,3] The mechanism proposed by Dyke and Higginson[3] for these reactions is nucleophilic attack at the halide ion by the free carboxylate group, aided by the accelerating metal ion which holds the halide and carboxylate groups in close proximity.

The replacement of azide ion by H_2O in $[Co(NH_3)_5N_3]^{2+}$ and $[Cr(H_2O)_5N_3]^{2+}$ is accelerated by HNO_2.[6,7] These reactions are believed to proceed *via* oxidation of coordinated N_3^- by NO^+, with subsequent rapid leaving of N_2. A somewhat similar reaction is the iodine-catalyzed aquation of $[Cr(H_2O)_5I]^{2+}$, which appears to involve oxidation of coordinated iodide ion as shown in eq 1 and 2.[8]

$$[Cr(H_2O)_5I]^{2+} + I_2 \overset{\text{rapid, reversible}}{\rightleftarrows} [Cr(H_2O)_5I_2]^{3+} + I^- \qquad (1)$$

$$[Cr(H_2O)_5I_2]^{3+} \xrightarrow{\text{slow}} [Cr(H_2O)_6]^{3+} + I_2 \qquad (2)$$

This report describes the effect of the presence of molecular bromine upon reaction 3. It will be seen that Br_2 accelerates the ring closure in eq 3 in a first-order manner

$$[Co^{III}(EDTA)Br]^{2-} \xrightarrow{k_{rc}} [Co^{III}EDTA]^- + Br^- \qquad (3)$$

but that Br_3^- does not have this effect. The concentration of bromide ion does not affect the acceleration by Br_2. It appears that reaction 3 is accelerated by direct electrophilic attack of Br_2 upon the coordinated bromide ion.

Experimental Section

The reactions were followed using a Cary 16 spectrophotometer interfaced to a Varian G-2000 recorder. The wavelengths monitored were 540 nm (λ_{max} for $[Co^{III}EDTA]^-$, ϵ 338 M^{-1} cm^{-1}) and 590 nm (λ_{max} for "isomeric" $[Co^{III}(EDTA)Br]^{2-}$, ϵ 234 M^{-1} cm^{-1}).[4] The ring-closure reactions (eq 3) were observed subsequent to the oxidation of $[Co^{II}EDTA]^{2-}$ by bromine. The kinetics of the latter reaction are described elsewhere.[9]

Bromine solutions were prepared by dissolving elemental bromine in a solution containing the appropriate concentration of sodium bromide and approximately 10^{-3} M $HClO_4$. The solutions were standardized spectrophotometrically at the isosbestic point of Br_2 and Br_3^- (λ 457 nm, ϵ 98 M^{-1} cm^{-1}) immediately prior to an experiment. Standard solutions of $[Co^{II}EDTA]^{2-}$ were prepared by direct weighing of $Na_2Co^{II}EDTA \cdot 2H_2O$, which was isolated using the method of Schwarzenbach and Parissakis.[10] Sodium perchlorate was recrystallized twice before use.

Temperature was maintained at 25.0 ± 0.1° for all experiments. Spectra to identify the species were taken using a Cary 14 spectrophotometer. Measurements of pH were made using an Instrumentation Laboratories Model 245 pH meter with a reference electrode containing saturated NaCl.

Results

The observed kinetics of the ring closure of $[Co^{III}(EDTA)Br]^{2-}$ at various initial concentrations of bromide ion and bromine, $[Br^-]_T$ and $[Br_2]_T$, are given in Table I. The $[Br_2]_T$ is equal to $[Br_2]$ + $[Br_3^-]$ and these species are in rapid equilibrium. The notation k_{rc} refers to the observed first-order rate constant for the ring closure of the complex under the conditions given. That the value of k_{rc} depends upon the concentration of molecular bromine, $[Br_2]$, but not upon $[Br_2]_T$, can be seen from Table I. At a given total bromine concentration, increasing bromide ion concentration decreases the value of k_{rc}, but this is simply due to the decreased fraction of $[Br_2]_T$ represented by $[Br_2]$. There is no detectable inhibition by bromide ion of the effectiveness of Br_2 in accelerating the ring-closure reaction.

Table I. Observed Kinetics of the Bromine-Accelerated Ring Closure of $[Co^{III}(EDTA)Br]^{2-}$ [a]

$[Br_2]$, M	$[Br^-]_T$, M	$[Br_2]_T$, M	λ, nm	k_{rc}, sec^{-1}
0.025	0.25	0.098	540	7.0×10^{-4}
0.018	0.08	0.036	590	4.5×10^{-4}
0.0092	0.25	0.043	540	2.7×10^{-4}
0.0092	0.25	0.043	590	2.6×10^{-4}
0.0035	0.58	0.035	540	1.35×10^{-4}
0.0032	0.29	0.018	590	7.8×10^{-5}
0.0018	0.54	0.018	540	7.7×10^{-5}
0.00097	1.04	0.018	590	2.6×10^{-5}
0.00043	1.02	0.0078	590	2.8×10^{-5}

[a] $[CoEDTA]_T = 1.00 \times 10^{-3}$ M; $\mu = 1.1$ ($NaBr + NaClO_4$); acetate buffer, pH 3.5; Br_3^- formation constant = 16.85 M^{-1}: J. M. Pink, *Can. J. Chem.*, 48, 1169 (1970).

Figure 1 shows the dependence of k_{rc} upon the concentration of molecular bromine. The slope of the least-squares straight line is $(2.6 \pm 0.1) \times 10^{-2}$ M^{-1} sec^{-1} and is designated k_a denoting the Br_2 acceleration of the ring closure. The intercept of Figure 1 is $(2 \pm 1) \times 10^{-5}$ sec^{-1}.

Discussion

The product of the oxidation of $[Co^{II}EDTA]^{2-}$ by bromine occurs in two isomeric forms, one with the bromide ion trans to a nitrogen atom of EDTA ("trans-N" isomer) and another in which the bromide ion is trans to a coordinated carboxyl group ("trans-O" isomer).[1,4] The normal product distribution for the oxidation of $Co^{II}L^{2-}$ by bromine is 45% trans-N isomer.[4] This mixture of the trans-N and trans-O isomers is called "isomeric" $[Co^{III}(EDTA)Br]^{2-}$.

The two isomers have been shown to undergo ring closure at different rates.[1,4] The rate constant for the ring closure of the trans-N isomer is 2.0×10^{-5} sec^{-1} and that of the trans-O isomer is 3.0×10^{-6} sec^{-1}, both determined in the absence of bromine and accelerating cations.[4] It is noted that the uncatalyzed rate constant for the trans-N isomer is equal to the intercept of Figure 1. The rate constant for the ring closure of the trans-O isomer is slightly outside the experimental error of this intercept.

In the present study only one ring-closure reaction is observed. The ring closure is observed subsequent to the oxidation of $[Co^{II}EDTA]^{2-}$; however, some ring closure takes place during the time span of the oxidation. The absorbance change (due to the accelerated ring closure) which is actually observed, after the completion of the oxidation reaction, approaches 80% of the predicted ΔA for the ring closure reaction if the reactant were the isomeric mixture. If the reactant were only the trans-N isomer the ΔA observed approaches 100% of that predicted.[4] It is possible that the isomeric composition of $[Co^{III}(EDTA)Br]^{2-}$ depends upon the conditions under which the oxidation is performed and that under the present conditions the product is mostly one isomer (probably trans-N). Another possibility is that bromine accelerates an interconversion of the trans-N and trans-O isomers such that the two isomers interconvert rapidly compared to the ring-closure reaction. In this case only the ring closure of the trans-N isomer would be observed.

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(4) B. Grossman, Ph.D. Thesis, State University of New York at Buffalo, 1969.

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(6) A. Haim and H. Taube, *Inorg. Chem.*, 2, 1199 (1963).

(7) R. C. Thompson and E. J. Kaufman, *J. Amer. Chem. Soc.*, 92, 1540 (1970).

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

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

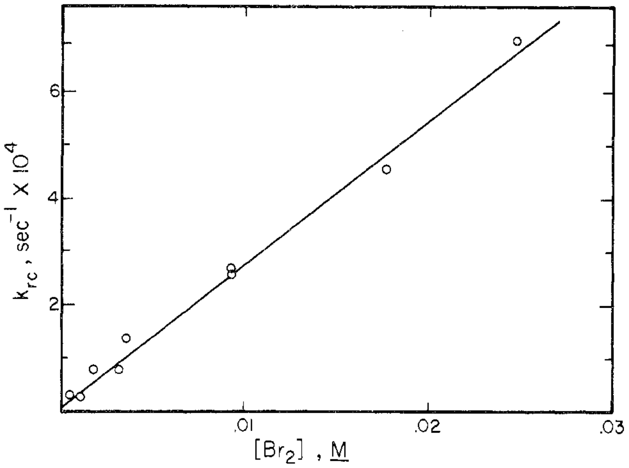

Figure 1. Dependence of k_{rc} upon the concentration of molecular bromine. The slope, k_a, is $(2.6 \pm 0.1) \times 10^{-2}\ M^{-1}\ \mathrm{sec}^{-1}$. The intercept is $(2 \pm 1) \times 10^{-5}\ \mathrm{sec}^{-1}$.

The previous study which most closely parallels the present work is the aforementioned aquation of $[\mathrm{Cr(H_2O)_5I}]^{2+}$ in the presence of iodine.[8] Espenson observed inhibition by iodide ion of the acceleration (due to iodine) of the aquation reaction. The iodide inhibition requires a mechanism such as that shown in eq 1 and 2. This type of inhibition is not observed for bromide ion in the present study. It is therefore proposed that the acceleration of the ring closure of $[\mathrm{Co^{III}(EDTA)Br}]^{2-}$ is due to electrophilic attack of bromine upon the coordinated bromide ion, as shown in eq 4 and 5. The $\mathrm{Br_3}^-$ ion does not take part in direct

$$[\mathrm{Co^{III}(EDTA)Br}]^{2-} + \mathrm{Br_2} \xrightarrow{k_a} [\mathrm{Co^{III}EDTA}]^- + \mathrm{Br_3}^- \qquad (4)$$

$$\mathrm{Br_3}^- \overset{\text{very rapid}}{\rightleftarrows} \mathrm{Br_2} + \mathrm{Br}^- \qquad (5)$$

electrophilic attack on $[\mathrm{Co^{III}(EDTA)Br}]^{2-}$ as it is a poor electrophile for Br^- (*i.e.*, $\mathrm{Br_4}^{2-}$ is not a stable species).

The rate constant for the ring closure of $[\mathrm{Co^{III}(EDTA)OH_2}]^-$ is 1.8×10^{-3} sec^{-1} at 25.0°.[11] This is faster than the fastest k_{rc} value in Table I, 7.7×10^{-4} sec^{-1}. Therefore it is not possible on the basis of the present data to rule out the aquated intermediate prior to the ring-closure step. In any case electrophilic attack by $\mathrm{Br_2}$ accelerates the loss of coordinated Br^- from the cobalt(III) complex.

Registry No. $\mathrm{Co(EDTA)Br^{2-}}$, 28135-63-6; $\mathrm{Br_2}$, 7726-95-6.

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

[11] I. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 260 (1958).

Correspondence

Magnetic Properties of Hexaureacobalt(III) Perchlorate

Sir:

The preparation and properties of the title compound have recently been described by Bennett.[1] Of particular interest is the observation of a residual paramagnetism at 20°, corresponding to an effective magnetic moment of 0.95 BM considerably in excess of that expected for temperature-independent paramagnetism for low-spin Co(III) compounds.[2] It was suggested that since oxygen-coordinated urea occupies a lower spectrochemical position than water, the anomalously high paramagnetism might be due to a sufficiently close approach to the spin crossover for the high-spin state to be measurably populated at this temperature. Although spin isomerism is known for Co(II) complexes in both five- and six-coordinate geometries[3] there are as yet no known instances of the phenomenon in Co(III) compounds. We were therefore stimulated to investigate this compound further by magnetic susceptibility measurements by the Gouy method over a wide temperature range.

The complex was prepared as described by Bennett and characterized by elemental analyses. *Anal.* Calcd for $\mathrm{C_6H_{24}N_{12}O_{18}Cl_3Co}$: C, 10.0; H, 3.2; N, 23.4; Cl, 14.8; Co, 8.2. Found: C, 9.9; H, 3.3; N, 23.0; Cl, 15.4; Co, 8.0. Ir and uv-visible spectra agreed with those previously reported.[1] All measurements were made in an atmosphere of oxygen-free nitrogen.

Samples from three separate preparations showed essentially the same behavior though differing initial room-temperature moments, within the range 1.2-1.8 BM, were found for them. The susceptibilities are independent of the applied field strength. All samples showed an increasing paramagnetism as a function of time. The rate of change, negligible below 293°K, increased with increase in temperature. At 373°K the moment changed from the initial value to a final value of *ca.* 5.0 BM (calculated on the molecular weight of the parent compound) within 20 hr; no further change occurred on maintaining this temperature for a further 48 hr. The increase in paramagnetism was accompanied by a small loss in weight (*ca.* 3.0% in all) of the sample. The rates of change of susceptibility and of weight paralleled each other closely and no further change in weight was observed after the magnetic properties became constant. Freshly prepared samples, and samples incompletely decomposed by maintaining them at *ca.* 353°K for a few hours, obeyed the Curie-Weiss law over the temperature range 90-273°K with a Weiss constant (negative temperature intercept) of 17-25°. Samples which had been completely aged by maintaining them at 373°K for more than 48 hr also showed Curie-Weiss behavior, this time over the complete temperature range studied, 90-373°K.

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[3] See E. K. Barefield, D. H. Busch, and S. M. Nelson, *Quart. Rev., Chem. Soc.*, 22, 457 (1968); W. S. J. Kelly, G. H. Ford, and S. M. Nelson, *J. Chem. Soc. A*, 388 (1971); W. V. Dahlhoff and S. M. Nelson, *ibid.*, 2184 (1971).