ing (lone pair) electrons in the p orbital which is orthogonal to the plane of the ligands make a contribution to the field gradient tensor which almost compensates for the contributions of the p electrons involved in the metal–ligand interactions. The resulting charge distribution has nearly (but not identically) cubic symmetry around the metal atom as inferred from the magnitude of the QS parameter which is observed. The small (but significant) increase in QS as the halogen electronegativity decreases and size increases may be related to the change in hybridization referred to above and reflects the departure from orthogonality of the p-electron population. A more detailed interpretation of the presently available data does not seem warranted at the present time.

Experimental Section

The three tin oxyhalides were prepared by literature methods[10] by the ozonization of the anhydrous tetrahalides and mounted as solid samples ($\sim$10 mg of Sn/cm^2) in standard sample holders. The constant-acceleration Mössbauer spectrometer has been described earlier[12] and was calibrated using NBS 0.8-mil 99.9% natural iron foil. The sample temperatures were 80 ± 1°K by calibrated thermocouple. All ^{119}Sn spectra were run using a room-temperature $BaSnO_3$ source, and zero relative velocity was determined experimentally from a room-temperature $BaSnO_3$–$BaSnO_3$ spectrum. Spectra were computed by using a standard curve-fitting program[11] in which the two line widths (but not intensities) were assumed to be identical. The straight lines shown in Figure 1 represent least-squares fits to the data.

Acknowledgments.—This research was supported in part by the U. S. Atomic Energy Commission (Document NYO 2472-73) and the Petroleum Research Fund, administered by the American Chemical Society. This support is herewith gratefully acknowledged.

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[12] See Chapter by N. Benczer-Koller and R. H. Herber in ref 2.

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Substitution Reactions of Oxalato Complex Ions. IX. The Kinetics of the Anation Reaction of Aquohydroxobis(ethylenediamine)cobalt(III) Ion by Oxalate in Basic Aqueous Solution

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Received September 30, 1970

The preceding paper in this series[2] reported the results of a study of the reactions in strongly acidic solutions (pH <1) of the system analogous to that of the present study, where, however the reactants were limited essentially to *cis*-$Co(en)_2(H_2O)_2^{3+}$ (en = ethylenediamine) and the two oxalate species $H_2C_2O_4$ and $HC_2O_4^-$. As one shifts to higher pH, the system exhibits much greater complexity due to the various acid–base and cis–trans equilibria of the diaquo complex, as first elucidated by Bjerrum and Rasmussen[3] and recently further clarified by Lincoln and Stranks[4] in a phosphate anation study. Above pH 7, the only oxalate species present in measurable amount is $C_2O_4^{2-}$, while the reactant complex is made up of a mixture of the cis and trans forms of the ions $Co(en)_2(H_2O)(OH)^{2+}$ and $Co(en)_2(OH)_2^+$ as defined by the appropriate equilibrium constants.[3,4]

It was previously predicted[2] that the mechanism of oxalate anation in solutions of low acidity should be according to the reactions

$$Co(en)_2(H_2O)(OH)^{2+} + C_2O_4^{2-} \rightleftarrows Co(en)_2(H_2O)(OH)^{2+}\cdot C_2O_4^{2-} \qquad K_{IP} \quad (1)$$

$$Co(en)_2(H_2O)(OH)^{2+}\cdot C_2O_4^{2-} \longrightarrow Co(en)_2(OH)(C_2O_4) + H_2O \qquad k_0 \quad (2)$$

$$Co(en)_2(OH)(C_2O_4) \longrightarrow Co(en)_2C_2O_4^+ + OH^- \qquad k_1 \quad (3)$$

Further, it was predicted that the hydroxooxalato intermediate formed in reaction 2 would prove to be identifiable, in contrast to the related aquooxalato species which was assumed to appear as an intermediate in the acidic system. The latter species is related to the uncharged complex by the equilibrium

$$Co(en)_2(H_2O)(C_2O_4)^+ + H_2O \rightleftarrows Co(en)_2(OH)(C_2O_4) + H_3O^+ \qquad K_a \quad (4)$$

The predictions were based on the known very much higher lability of the hydroxoaquo complex as compared to the diaquo[5] and the greater difficulty of dislodging hydroxide as compared to water ligand, suggesting that reaction 3 would take place less rapidly than its analog in acidic solution

$$Co(en)_2(H_2O)(C_2O_4)^+ \longrightarrow Co(en)_2C_2O_4^+ + H_2O \qquad k_2 \quad (5)$$

In the present work, the anation has been studied in the range $7.3 < pH < 9.9$ and the uncharged complex compound $Co(en)_2(OH)(C_2O_4)$ has been identified in agreement with expectation. In addition, rate constants of some of the possible reactions have been determined and some suggestions made concerning the stereochemistry of these processes. The results, together with those obtained in an earlier study[6] of the reverse of reaction 3, enable a reasonably complete mechanistic assessment of this anation–hydrolysis system over a wide range of pH.

Experimental Section

Aquohydroxobis(ethylenediamine)cobalt(III) nitrate was prepared by standard procedure.[7] To observe the rate of appearance of the nonionic unidentate oxalato intermediate, a weighed quantity of the aquohydroxo salt was dissolved in a known volume of water previously brought to reaction temperature.[8,9] This solution was mixed with a known volume of sodium oxalate solution of the desired concentration, appropriately buffered at the same temperature, and with its ionic strength adjusted with sodium nitrate. Samples were withdrawn at regular time intervals and passed through a column of mixed ion-exchange resin.[10] The effluent and pure-water washings, containing only the uncharged $Co(en)_2(OH)(C_2O_4)$ complex, were acidified, made up to a known volume, and allowed to stand overnight before analysis

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[1] University Research Fellow, State University of New York at Buffalo, 1968; on leave from the Department of Chemistry, University of Hong Kong.

[2] Part VIII: P. M. Brown and G. M. Harris, *Inorg. Chem.*, **7**, 1872 (1968).

[3] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

[4] S. F. Lincoln and D. R. Stranks, *Aust. J. Chem.*, **21**, 1745 (1968).

[5] W. Kruse and H. Taube, *J. Amer. Chem. Soc.*, **83**, 1280 (1961).

[6] S. Sheel, D. T. Meloon, and G. M. Harris, *Inorg. Chem.*, **1**, 170 (1962).

[7] The material used was obtained in this laboratory by Dr. P. M. Brown by crystallization from an aqueous solution of *cis*-$Co(en)_2(H_2O)(OH)(NO_3)_2$. The latter was prepared by neutralizing *cis*-$Co(en)_2(H_2O)_2(NO_3)_3$ with 1 equiv of NaOH (see ref 2 for preparation methods of the diaquo species).

[8] The aquohydroxo complex is of course in cis–trans equilibrium in an approximately 60:40 ratio. This equilibration is very rapid.[9]

[9] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).

[10] The mixed-bed column consisted of Dowex 50W-X8 resin in the Na^+ form and Dowex 1-X8 in the NO_3^- form, 20–50 mesh.

for the final product ion, $Co(en)_2C_2O_4^+$, by absorbance measurement at 500 nm.[11] In all runs, the concentration of oxalate was considerably in excess of complex so pseudo-first-order kinetics were observed for the formation reaction of the hydroxooxalato intermediate. In later experiments it was found possible to make the separation with cation-exchange resin alone. This single resin was therefore used except in runs where it was desired specifically to avoid the presence of oxalate ion in the effluent.

The kinetics of disappearance of the unidentate oxalato intermediate was followed by a similar technique. A solution of the intermediate was prepared *in situ* and brought to the desired pH, ionic strength, and temperature. As soon as thermal equilibrium was established, the first sample was withdrawn and treated as the zero-time sample. The effluent and washings from ion-exchange column treatment[12] now contained only unreacted intermediate, since the products of its reactions were cationic and remained on the column. Determination of the composition of the ionic products was effected by selective elution from the column after removal of the nonionic intermediate by thorough washing with water. The column was acidified with dilute acetic acid and the $Co(en)_2C_2O_4^+$ was quantitatively eluted with 1 M $NaNO_3$ and determined spectrophotometrically using the known absorbance data.[11] The other component of the acidified product, a cis–trans mixture of $Co(en)_2(H_2O)_2^{3+}$, was eluted with 3 M $NaNO_3$ and also determined spectrophotometrically. Final product distribution was determined by performing the separation on reactant solutions which have aged for 4 half-lives or more. Sodium hydroxide–boric acid buffers[13] were used to establish the pH of the solutions, measurement of which was made with a Beckman Research model meter. Complete spectral measurements over a range of wavelengths were made with a Cary Model 15 instrument, while fixed-wavelength measurements were made with a Beckman DU equipped with a Gilford digital readout accessory.

Results and Discussion

Preliminary experiments clarified the basic chemistry of the system. First, a self-buffered solution 0.01 M in complex ion and 0.1 M in sodium oxalate at an initial pH of 7.3 was allowed to stand at 25° for 2.5 hr before passage through the mixed-bed ion-exchange column. Cobalt analysis of effluent and washings showed that 93% of the product complex passes through unadsorbed. This nonionic species has a spectrum which corresponds closely to that of the product obtained fleetingly in the previous study[2] in a similar experiment at pH 5.5. After long standing (half-life of ~52 hr), during which the pH slowly increased to a final value of 7.8, an ionic product identifiable by its spectrum as $Co(en)_2C_2O_4^+$ is obtained. It is clear that the nonionic intermediate compound is $Co(en)_2(OH)(C_2O_4)$ as expected from the reaction sequence outlined earlier. Acidification of a solution of the nonionic intermediate produces the cationic entity[14] $Co(en)_2(H_2O)(C_2O_4)^+$ according to the equilibrium of eq 4. A pH titration indicated that the gross value of pK_a is 6.7 at 25°. The half-life for ring closure of the aquooxalato species according to eq 5 is about 2.5 hr at 25°, while at 60° the conversion to $Co(en)_2C_2O_4^+$ is complete in a few minutes.[15]

In another preliminary experiment, the solutions were buffered at a pH of 9.9 at 25°, when anation of the complex by oxalate is very much slower (half-life ~35 hr in 0.1 M oxalate) than in the $7 < pH < 8$ range. Some experiments at pH 9.9 and 50° showed that the anation did not proceed to completion, the fractions of hydroxooxalato product formed on long standing being 28 and 43% in 0.05 and 0.1 M $Na_2C_2O_4$, respectively. There being no evidence of ring closure under these conditions to produce $Co(en)_2C_2O_4^+$, the equilibrium observed here must be

$$Co(en)_2(OH)(C_2O_4) + OH^- \rightleftarrows Co(en)_2(OH)_2^+ + C_2O_4^{2+} \qquad K_b \quad (6)$$

The two sets of data lead to values for K_b of 510 and 530, respectively (pK_w = 13.3 at 50°).

The rate of appearance of the uncharged hydroxooxalato intermediate was now investigated as a function of oxalate concentration at 25° and an ionic strength of 0.32 M. The pH of each self-buffered solution was initially 7.3 and remained constant to within 0.1 unit during the first half-life of reaction. The k_{obsd} values are derived from the initial slopes of the conventional first-order plots to avoid the complications of the pH drift. It was found that a nonlinear relationship exists between rate and concentration of nucleophile such as is regularly observed in anation of complex aquo cations. This is readily explainable in terms of the ion-pair interchange mechanism as proposed in reactions 1 and 2, for which the analytical relationship is of the form[4]

$$1/k_{obsd} = 1/k_0 + 1/k_0K_{IP}[C_2O_4^{2-}] \qquad (7)$$

A plot of the k_{obsd} data in this reciprocal fashion gives a good straight line from which one readily derives values of k_0 and K_{IP} by use of the slope and intercept. Other series of experiments of this type were performed at 25°, ionic strength 0.37 M, and pH's of 7.3, 7.8, and 8.1 to yield the data presented in Table I. In this, the values of k_0(cor) are derived by dividing k_0 by f, the latter being the fraction of aquocobalt(III) complex which is in the form $Co(en)_2(H_2O)(OH)^{2+}$ at the specified pH.[3,4] The relative constancy of k_0(cor) indicates that only the monohydroxo species is reactive enough to anation to be observable under present conditions. This is understandable since the water-exchange data[5] for these complexes suggest that k_{ex} for the $(H_2O)(OH)$ type of complex, whether cis or trans, is $\sim 2 \times 10^{-3}$ sec^{-1} at 25° and low ionic strength, some 30 times more reactive at this temperature than any of the $(H_2O)_2$ or $(OH)_2$ species. The k_{ex} value quoted is seen to be about twice as great as k_0(cor), a similar relationship to that reported previously[2] for the corresponding constants in the anation of the diaquo complex by oxalate. There is

TABLE I
RATE OF FORMATION OF $Co(en)_2(OH)(C_2O_4)$ BY THE REACTION OF $Co(en)_2(H_2O)(OH)^{2+}$ ION WITH $C_2O_4^{2-}$ ION AT VARIOUS ACIDITIES[a]

pH	10^4k_0, sec^{-1}	K_{IP}, M^{-1}	f	10^4k_0(cor), sec^{-1}
7.3[b,c]	8.2	5.8	0.83	9.9
7.3[c]	7.2	5.5	0.83	8.7
7.8[d]	6.0	5.3	0.67	9.0
8.1[d]	5.0	5.7	0.50	10.0

[a] Temperature 25°; ionic strength 0.37 M; $[Co(en)_2(H_2O)(OH)^{2+}]_0$ = 0.004 M. [b] Ionic strength 0.32 M. [c] Self-buffered. [d] Borate buffer.

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[11] The following data for the various compounds were employed (wavelength maxima in nm first, molar extinction coefficient in M^{-1} cm^{-1} following): $Co(en)_2(OH)(C_2O_4)$, 510, 83; $Co(en)_2C_2O_4^+$, 500, 113; $Co(en)_2(H_2O)(C_2O_4)^+$, 500, 67; $Co(en)_2(H_2O)_2^{3+}$, 552, 31 (isosbestic point for cis and trans forms).

[12] The column used in this separation work consisted of Dowex 50W-X2 resin, 50–100 mesh.

[13] Borate buffers are quite unreactive to complexes of the type used in this work: see, for example, R. J. Dobbins and G. M. Harris, *J. Amer. Chem. Soc.*, **92**, 5104 (1970).

[14] The ion is formulated as given and not as $Co(en)_2(OH)(C_2O_4H)^+$ due to the known much higher basicity of ligand OH as compared to unidentate C_2O_4.

[15] This explains why the aquooxalato species was undetected in the anation in acidic solution in the 40–60° range.[2] Under the prevailing conditions of that study the half-life for *formation* of the cationic intermediate was of the order of 1 hr or more.

a considerable contrast with the anation rate of the aquohydroxo complex by phosphate,[4] where the water-exchange rate exceeds the ligand-interchange rate by a factor of between 10 and 20. Our K_{IP} value of only about 6 at 25° is somewhat lower than expected, since the corresponding constant for the $Co(en)_2(H_2O)_2{}^{3+}$–$HC_2O_4{}^-$ system is about 120 (40°) and for the $Co(en)_2(H_2O)(OH)^{2+}$–$HPO_4{}^{2-}$ system about 60 (22.5°). This may be related to the fact that the anions in the latter two systems are protonated, enabling a type of multiple H bonding not possible in the present system. It is of interest that the pseudo-second-order rate constants, $(k_0(\text{cor}))K_{IP}$, for oxalate and phosphate anation at low anion concentration are almost identical (5.2×10^{-3} M^{-1} sec^{-1} at 25° for $C_2O_4{}^{2-}$, 4.6×10^{-3} M^{-1} sec^{-1} at 22.5° for $HPO_4{}^{2-}$).

A study was next made of the rate of disappearance of the uncharged intermediate $Co(en)_2(OH)(C_2O_4)$, using freshly prepared solutions of the latter (0.004 M) in the presence of 0.05 M $Na_2C_2O_4$ at a total ionic strength of 0.37 M, temperatures of 40, 45, and 50°, and pH's of 7.8, 8.1, and 9.9. The rate constants k' (for $Co(en)_2C_2O_4{}^+$ formation by ring closure) and k'' (for oxalate displacement by OH^-) are derived by apportioning the observed pseudo-first-order rate constant between the products[16] according to the relative amounts of each (see Table II). The constant k_2 is derived from k' on the assumption that *all* ring closure is according to reaction 5, whence $k_2 = k'f'$, where f' is the fraction[17] of unidentate oxalato complex in the form $Co(en)_2(H_2O)(C_2O_4)^+$. To calculate k_3, it is assumed that oxalate displacement is first order in base concentration, so $k_3 = k''/[OH^-]$.

TABLE II

RATE OF DISAPPEARANCE OF $Co(en)_2(OH)(C_2O_4)$ AT IONIC STRENGTH 0.37 M AND VARIOUS TEMPERATURES AND ACIDITIES

pH	$10^5k'$, sec^{-1}	$10^5k''$, sec^{-1}	10^3k_2, sec^{-1}	k_3, M^{-1} sec^{-1}
		40°		
7.8	2.3	0.1	0.5	0.4
8.1	1.4	0.15	0.6	0.3
9.9	...	7.9	...	0.3
		45°		
7.8	4.1	0.2	0.9	0.8
8.1	2.6	0.3	1.1	0.6
9.9	...	15.3	...	0.5
		50°		
7.8	7.2	0.4	1.5	1.6
8.1	4.5	0.6	1.9	1.2
9.9	...	30.0	...	1.0

It is seen that the various k_2 and k_3 values at a given temperature are reasonably in agreement, considering the uncertainties inherent in the estimates. The respective temperature parameters are $\Delta H_2{}^{\ddagger} = 23.0 \pm 0.5$ kcal/mol, $\Delta S_2{}^{\ddagger} = -6.5 \pm 1.0$ cal deg^{-1} mol^{-1}, $\Delta H_3{}^{\ddagger} = 27 \pm 1$ kcal/mol, and $\Delta S_3{}^{\ddagger} = 8 \pm 2$ cal deg^{-1} mol^{-1}. Extrapolation of k_2 to 25° suggests a value of around 10^{-4} sec^{-1} for this constant at the lower temperature, consistent with our preliminary estimate of a half-time for ring closure of the aquooxalato species of 2.5 hr. An extrapolation of k_3 to 71° yields a value of 15 M^{-1} sec^{-1} so that it is easily understandable that no evidence for intermediate formation of unidentate oxalato species was discernible in our study[6] of the base-catalyzed hydrolysis of $Co(en)_2C_2O_4{}^+$. The rate constant for the first step of this reaction, the reverse of reaction 3, is 2.7×10^{-2} M^{-1} sec^{-1} at 71°, less than 0.002 as rapid as the second step defined by k_3.

Finally, some remarks need to be made concerning the stereochemistry of the various processes which have been considered. We are unable to deduce from our evidence whether it is the cis or trans form of the aquohydroxo complex which is involved in reactions 1 and 2. However, this is of little concern in the evaluation of our constants, since the two forms are present in approximately equal amounts (the cis/trans ratio is 1.4 over a wide temperature range[4]) and the rate of equilibration of these stereoisomers is much more rapid than those of any of the other reactions under consideration (equilibration half-time is 2.3 min[9] at 25°). Also, as already pointed out, the water-exchange rates of the two forms are almost identical,[5] so one would expect them to be equally reactive in dissociative interchange. As to the geometry of the product $Co(en)_2(OH)(C_2O_4)$, one can argue that it is nearly all in the cis configuration since ring closure to give $Co(en)_2C_2O_4{}^+$ is essentially complete up to pH 8.1, a reaction which is impossible for the trans isomer. The spectral data also tend to favor the cis configuration as the major constituent, since the molar extinction coefficient of $Co(en)_2(OH)(C_2O_4)$ at the maximum in the 500-nm region (83) is not far from that of *cis*-$Co(en)_2(OH)_2{}^+$ (93) but differs substantially from that of the trans analog (41). However, the cis–trans isomerization of the $Co(en)_2(OH)(C_2O_4)$ complex may be as rapid (through its protonated aquooxalato form) as is the corresponding reaction of the aquohydroxy species. In this event, the ring-closure reaction could always occur through the cis isomer without any limitation by the rate of the trans to cis conversion.

Acknowledgment.—Financial support of this research by the National Science Foundation (Grant No. GP-6708) and by the Graduate School of the State University of New York at Buffalo is gratefully acknowledged.

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[16] At the lower pH's, the concentration ratio of the products in any given run is constant with time, indicating a parallel first-order reaction system. At pH 9.9, reaction 6 is the only observable process, and k'' is derived by treating the data as belonging to a pseudo-first-order equilibration.

[17] For the purposes of this calculation, the value of pK_a is estimated to be about 6.5 in the 40–50° range (using a ΔH value of 4 kcal/mol as suggested by Lincoln and Stranks[4] for this type of acid–base equilibrium).

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Novel Synthesis of Difluorophosphine Oxide, F_2HPO

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Received October 5, 1970

Difluorophosphine oxide, F_2HPO, was first characterized and reported by Treichel, Goodrich, and Pierce[1]

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[1] P. M. Treichel, R. A. Goodrich, and S. B. Pierce, *J. Amer. Chem. Soc.*, **89**, 2017 (1967).