Contribution from the Department of Chemistry, Western Washington State College, Bellingham, Washington 98225

Reactions of Ethylenediamine-*N*,*N'*-diacetatodiaquo Complexes of Cobalt(III). 2. Oxalate Anation of the α-Cis Isomer in Highly Acidic Aqueous Medium[1]

John A. Weyh,* Richard B. Maynard, and Timothy J. Baker

Received January 26, 1976 AIC60070O

In an earlier paper[1] we described the oxalate anation of α-*cis*-ethylenediamine-*N*,*N'*-diacetatodiaquocobalt(III) ion (α-*cis*-Co(EDDA)$(OH_2)_2^+$) in slightly acidic aqueous media. The product of the reaction was 100% β-*cis*-Co(EDDA)$(C_2O_4)^-$. Our proposed mechanism involved initial ion-pair equilibration followed by rate-determining substitution. We wish to report here our anation studies involving the same reactants except that they were carried out in highly acidic aqueous media.

There were a number of reasons for conducting this study. First, the product of the reaction in highly acidic media is 100% α-*cis*-Co(EDDA)$(C_2O_4)^-$ rather than the β-cis isomer. Second, in slightly acidic media[1] it was proposed that Co(EDDA)(OH)$(OH_2)^0$ made an important contribution to the generation of product. The noncommon intercept of k_{obsd}^{-1} vs. C_{ox}^{-1} plots (C_{ox} = total oxalate concentration) as a function of pH was ascribed to the presence of this species. In highly acidic media Co(EDDA)(OH)$(OH_2)^0$ is not present and a common intercept should be obtained for such plots if our initially proposed mechanism is correct. Finally, several anation studies[2-5] of cobalt(III) complexes involving various carboxylic acids and carboxylate anions have been reported since our initial work. These suggest that "ion-pair" equilibration is not a factor between complex and neutral carboxylic acid if only one replaceable H_2O ligand is available on the complex. Our complex has two cis aquo ligands.

Experimental Section

Ethylenediamine-*N*,*N'*-diacetic acid was used as received from Pfaltz and Bauer, Inc. All other chemicals were reagent quality. Distilled water was used throughout.

α-*cis*-[Co(EDDA)$(OH_2)_2$]ClO_4 was prepared as previously described.[1]

Kinetic studies were made using a Coleman Perkin-Elmer Model 46 spectrophotometer equipped as previously described.[1] Rate constants were determined at 383 nm. This corresponds closely to a peak position for both reactant and product with the molar absorptivities being 75[6] and 143,[7] respectively. "Infinite" absorbance measurements were made after at least 10 half-lives, and these readings were checked intermittently for constancy. The complex concentration was 2.50×10^{-3} M in all of the experiments reported.

The procedure for a typical kinetic run is outlined as follows. The proper amount of oxalic acid, ensuring pseudo-first-order kinetics, was weighed into a flask. Then sodium nitrate and nitric acid were added to control the ionic strength ($\mu = 0.50$) and the acidity. Finally distilled water was added to mark. This solution was cooled to 0 °C and the complex added. Portions of the prepared solution were placed in 5-ml ampules and the ampule tops sealed in a flame. The samples were then placed in a water bath. After temperature equilibration, samples were removed periodically, quenched in an ice bath, and allowed to come to room temperature, and the absorbance was read. The reference cell contained H_2O.

Results and Discussion

The product of the reaction in the acidity range studied (0.0500–0.500 M H^+), is geometrically pure α-*cis*-Co(EDDA)$(C_2O_4)^-$. This was established by spectral and ion-exchange studies. At $[H^+] \simeq 3.0 \times 10^{-3}$ M a mixture of α- and β-cis product is detected and at pH 5 the product is the β-cis isomer.

A series of kinetic runs was made systematically varying $[H^+]$, C_{ox}, and temperature. In all cases plots of $-\log (A_\infty - A_t)$ vs. time were linear for several half-lives.

Table I. Pseudo-First-Order Rate Constants for Reaction of α-*cis*-Co(EDDA)$(OH_2)_2^+$ with $H_2C_2O_4$ and $HC_2O_4^-$ ($\mu = 0.50$): $10^5 k_{obsd}$, s^{-1} (C_{ox}, M)

0.50 M H^+	0.10 M H^+	0.050 M H^+
	(a) 62.00 °C	
3.23 (0.0400)	5.98 (0.0500)	5.67 (0.0400)
3.87 (0.0500)	7.67 (0.0750)	6.70 (0.0500)
5.33 (0.0750)	9.03 (0.100)	7.97 (0.0700)
6.08 (0.100)	11.8 (0.200)	9.27 (0.0900)
9.42 (0.200)		
	(b) 69.00 °C	
6.47 (0.0400)	8.96 (0.0333)	12.5 (0.0400)
8.03 (0.0500)	12.5 (0.0500)	14.5 (0.0500)
10.6 (0.0750)	16.3 (0.0750)	17.9 (0.0700)
12.9 (0.100)	19.2 (0.100)	20.6 (0.0900)
20.5 (0.200)	27.4 (0.200)	
	(c) 75.00 °C	
12.8 (0.0400)	26.2 (0.0500)	25.4 (0.0400)
15.4 (0.0500)	33.4 (0.0750)	30.0 (0.0500)
20.4 (0.0750)	40.4 (0.100)	36.7 (0.0700)
26.2 (0.100)	57.4 (0.200)	40.7 (0.0900)
40.2 (0.200)		

Scheme I

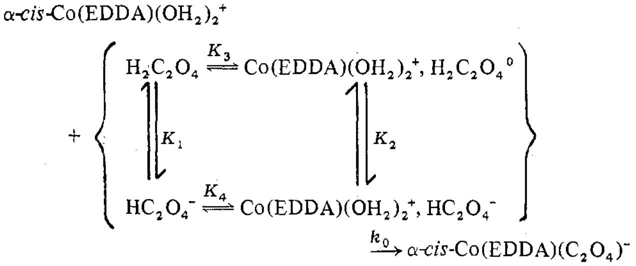

Table I lists the various values of k_{obsd} obtained as a function of C_{ox}, $[H^+]$, and T. Duplicate runs generally gave k_{obsd} values that agreed within 2–3%. Hydrogen ion concentration affects k_{obsd} in an inverse fashion. Further, as C_{ox} increases, k_{obsd} increases but not nearly in direct proportion. Such behavior has been interpreted as being indicative of ligand oxalate–reactant complex ion-pair equilibration prior to the rate-determining step.[1,2-5,8,9] This less than first-order dependence on C_{ox} is noted at all acidities studied indicating similar behavior by zero-charged $H_2C_2O_4$ and by $HC_2O_4^-$.

Plots of k_{obsd}^{-1} vs. C_{ox}^{-1} are linear at all acidities and temperatures studied. Further, for each temperature, the above plots have a common intercept but different slopes as determined by linear regression analysis. A mechanism which is in agreement with all of the experimental data for the $H_2C_2O_4$–$HC_2O_4^-$ anation of α-*cis*-Co(EDDA)$(OH_2)_2^+$ is shown in Scheme I. By appropriate substitution[10] the proposed mechanism yields the rate law

$$\frac{d[P]}{dt} = \frac{([H^+] + K_2)(k_0 K_3 C_{ox})}{[H^+] + K_1 + ([H^+] + K_2)K_3 C_{ox}} (C_{Co} - [P])$$

where P = α-*cis*-Co(EDDA)$(C_2O_4)^-$, $C_{ox} = [H_2C_2O_4] + [HC_2O_4^-]$, and $C_{Co} - [P]$ = concentration of all cobalt containing complexes which have not yet passed through the rate-determining step. From the rate law it is clear that

$$\frac{1}{k_{obsd}} = \frac{1}{k_0} + \frac{[H^+] + K_1}{k_0 K_3([H^+] + K_2)} \frac{1}{C_{ox}}$$

Hence plots of k_{obsd}^{-1} vs. C_{ox}^{-1} should be linear and exhibit a constant intercept at a constant T.

Both "ion pairs" are proposed to make the transition to product via the same rate constant k_0. This is dictated by the constant intercept obtained in the inverse plots. (Distinct rate

Table II. Values of Parameters Describing the α-*cis*-Co(EDDA)$(OH_2)_2^+$-$H_2C_2O_4$-$HC_2O_4^-$ System[a]

Temp, °C	10^4k_0, s^{-1}	K_2	K_3	K_4
62.00	1.77	0.24	4.9	20
69.00	4.33	0.34	2.9	16
75.00	8.55	0.37	2.8	18

[a] Uncertainties in the parameters reported here are related to the standard deviations in the various slopes and intercepts (as determined by linear regression analysis) as well as to the experimental error involved in the determination of k_{obsd}. Using these guidelines we report the relative uncertainty for k_0 as ±5-10% and that for K_2, K_3, and K_4 as ±10-20%.

constants for the two pairs predict a varying intercept with H^+.) Such behavior has been previously reported,[1,2,8,9] and in one case[2] where the data could be separated, rate constants identical within experimental error were obtained for two distinct ion pairs.

Using $K_1 = 6.0 \times 10^{-2}$ in the temperature range studied and obtaining k_0 from the intercept of the various k_{obsd}^{-1} vs. C_{ox}^{-1} plots, a simultaneous solution of the slope equations yields values for K_2, K_3, and K_4. Table II depicts the results of such treatment.

K_2 is larger than K_1 as would be expected simply on the basis of charge factors alone. Similar behavior has been noted in other systems.[1,8,11] K_4 is identical, within experimental error, with the value obtained for the α-*cis*-Co(EDDA)$(OH_2)_2^+$,-$HC_2O_4^-$ ion pair at 50.5 °C in slightly acidic media.[1] K_3 is considerably smaller than K_4 as would be expected on an electrostatic basis. Within experimental error, K_3 and K_4 exhibit negligible temperature dependence in the range studied.

It does appear that the ability of the prospective ligand to hydrogen bond to the reactant complex is an important factor in ion-pair formation for these systems. In the two systems[8] studied to date, where two aquo ligands cis to one another are available on the reactant complex, ion-pair formation is observed between the complex and $H_2C_2O_4$. In the cases where only one aquo ligand is available on the reactant complex, no ion-pair formation is observed involving the neutral carboxylic acid.[2-5] It should also be noted that the magnitude of the formation constants for similar ion pairs is much larger when two cis aquo ligands are available on the complex rather than one. As an example, for *cis*-Co(en)$_2(OH_2)_2^{3+}$,$HC_2O_4^-$ K_f = 119 at 40 °C,[8] whereas K_f values for the Co$(NH_3)_5$-$(OH_2)^{3+}$,$HC_2O_4^-$, $HCOO^-$, CH_3COO^-, and $CH_3CH_2COO^-$ ion pairs are 1.8 (50 °C),[2] 0.85 (60 °C),[3] 5.1 (60 °C),[4] and 4.4 (60 °C),[5] respectively. Similar extrapolations can be made to systems where the reactant complex is of lesser charge than 3+.[1]

The temperature variation in k_0 was used to calculate its activation parameters. Linear regression analysis yields the values $\Delta H^\ddagger = 27.5 \pm 1.0$ kcal/mol and $\Delta S^\ddagger = +6.3 \pm 2.8$ eu. These are essentially identical, within experimental error, with those obtained in the less acidic media.[1] Further, these values conform to the established pattern of activation parameters for similar, representative anation and water-exchange reactions (see ref 2, Table IV).

Extrapolation of k_0 to 50.50 °C using the above parameters indicates that k_0 in the present case is approximately one-fourth the value of k_0 obtained in slightly acidic media[1] where β-*cis*-Co(EDDA)$(C_2O_4)^-$ is the product. This decrease in rate constant may be due to the nature of the prospective ligand, i.e., $H_2C_2O_4$ and $HC_2O_4^-$ in the present case as compared to mainly $C_2O_4^{2-}$ in the less acidic media. It should be noted that removing the contribution of $HC_2O_4^-$ from the proposed mechanism in ref 1 does not allow a satisfactory fit of the reported data in that system. This might be expected, however, simply on the basis that removal of $HC_2O_4^-$ allows the use of three variable parameters instead of four for data fitting. Further, using the k_0 value obtained in the present study (extrapolated to the temperature under consideration in ref 1) does not allow a satisfactory fit of the data in ref 1. Hence we conclude that the k_0 values obtained at the two differing acidities are truly different.

The proposal in ref 1 that Co(EDDA)(OH)$(OH_2)^0$ plays an important role in generation of product in slightly acidic media seems borne out by the present study. The overall rate of reaction is much slower in the present study, as expected, and the attainment of a common intercept in the k_{obsd}^{-1} vs. C_{ox}^{-1} plots is as predicted.

The question related to the nature of product geometry as a function of pH still has not been satisfactorily answered. We are continuing our study of this general system, presently reacting the β-cis isomer of the parent diaquo complex with oxalate and malonate at various pH's.

Acknowledgment. J.A.W. wishes to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. α-*cis*-Co(EDDA)$(C_2O_4)^-$, 26135-70-6; α-*cis*-Co-(EDDA)$(OH_2)_2^+$, 26135-74-0.

References and Notes

(1) Part 1: J. A. Weyh, A. K. Newlun, T. J. Baker, and T. K. Shioyama, *Inorg. Chem.*, **12**, 2374 (1973).
(2) R. van Eldik and G. M. Harris, *Inorg. Chem.*, **14**, 10 (1975).
(3) P. R. Joubert and R. van Eldik, *Inorg. Chim. Acta*, **14**, 259 (1975).
(4) P. R. Joubert and R. van Eldik, *Inorg. Chim. Acta*, **12**, 205 (1975).
(5) P. R. Joubert and R. van Eldik, *J. Inorg. Nucl. Chem.*, **37**, 1817 (1975).
(6) K. Kuroda and K. Watanabe, *Bull. Chem. Soc. Jpn.*, **44**, 1034 (1971).
(7) K. Kuroda and K. Watanabe, *Bull. Chem. Soc. Jpn.*, **44**, 2250 (1971).
(8) P. M. Brown and G. M. Harris, *Inorg. Chem.*, **7**, 1872 (1968).
(9) H. Kelm and G. M. Harris, *Inorg. Chem.*, **6**, 706 (1967).
(10) Because of the circular nature of the various equilibria $K_2K_3 = K_1K_4$.
(11) (a) S. E. Ting, H. Kelm, and G. M. Harris, *Inorg. Chem.*, **5**, 696 (1966); (b) C. Andrade and H. Taube, *ibid.*, **5**, 1087 (1966).

Contribution from the Department of Chemistry,
Tulane University, New Orleans, Louisiana 70118

Electron Paramagnetic Resonance and Ligand Field Spectra of Vanadium(II) in Crystals of Cesium Calcium Trichloride. Spectroscopic Properties of a Perfectly Octahedral VCl_6^{4-} Complex

Gary L. McPherson* and Marc R. Freedman

Received January 28, 1976 AIC60074T

The double salts of the formula $M^IM^{II}X_3$ (where M^I is a univalent cation, M^{II} a divalent metal ion, and X a halide) have been the subject of numerous structural, spectroscopic, and magnetic investigations. The fluoride salts of this formula usually adopt some type of perovskite structure, while the salts of the other halides generally crystallize in one of several hexagonal lattices. Exceptions to this general trend are the chloride salts $CsCaCl_3$ and $CsSrCl_3$ which have been shown to be cubic perovskites.[1] A cubic perovskite can be described as an infinite three-dimensional array of octahedra sharing corners. Each divalent ion is surrounded by a regular octahedron of anions.

It has been found that $CsVCl_3$ is soluble in $CsCaCl_3$ to the extent that crystals which contain concentrations of V(II) large enough for spectroscopic observation can be prepared. Thus, it is possible to study the electronic structure of a VCl_6^{4-} complex that is perfectly octahedral. Previous spectroscopic investigations of divalent vanadium in chloride lattices have involved crystal systems in which the environment of the V(II) ion is significantly distorted from regular octahedral geometry.