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Anation of the *cis*-Diaqua(ethylenediamine)(oxalato)chromium(III) Complex Ion by Oxalate Species

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At pH 5 and 35.0 °C the *cis*-Cr(C₂O₄)(NH₂CH₂CH₂NH₂)(H₂O)₂⁺ complex ion undergoes anation by oxalate species in aqueous solution to produce Cr(C₂O₄)₂(NH₂CH₂CH₂NH₂)⁻ and small quantities of Cr(C₂O₄)₂(NH₂CH₂CH₂NH₃)(H₂O). The products of the anation reaction are unstable in this pH region and in turn undergo a series of reactions which leads ultimately to Cr(C₂O₄)₃³⁻. The kinetics of the initial anation reaction have been investigated at temperatures from 20.0 to 40.0 °C, at pH values from 2.00 to 5.00, at formal oxalate concentrations from 0.050 to 0.300 F and at ionic strengths of 0.80 and 1.00 M in potassium nitrate media. Observed pseudo-first-order rate constants exhibit a complex hydrogen ion dependence and a mass law retarded first-order dependence on the formal oxalate concentration. These rate constants have been interpreted in terms of a mechanism in which ion pair formation between HC₂O₄⁻ (K_B), C₂O₄²⁻ (K_C) and the parent complex precede a common ligand interchange step (k₁). In general, $k_{\text{obsd}} = k_1 K_C [H^+] ([H^+] + K_2') [C_2O_4^{2-}] / \{ K_2' ([H^+] + K_{a1}) + K_C [H^+] ([H^+] + K_2') [C_2O_4^{2-}] \}$, where K₂' is the acid dissociation constant of an associated hydrogen oxalate ion and K_{a1} is the first acid dissociation constant of the aqua ligands of the complex ion. At 25.0 °C and an ionic strength of 0.80 M, pK_{a1} = 5.92, K₂' = (7.25 ± 0.15) × 10⁻⁴ M, K_B = 1.35 M⁻¹, K_C = 4.70 ± 0.08 M⁻¹, and k₁ = (1.44 ± 0.05) × 10⁻³ s⁻¹. In the stated temperature interval and at an ionic strength of 0.80 M, the activation parameters of k₁ were found to be ΔH[‡] = 18.1 ± 0.4 kcal mol⁻¹ and ΔS[‡] = -10.7 ± 1.4 cal mol⁻¹ K⁻¹. A two-step oxalate anation mechanism has been described for this complex ion and other oxalato complexes of chromium(III). The mechanism is initiated by one-ended dissociation and isomerization of an oxalato-*O,O'* ligand to the oxalato-*O,O* bonding mode. Associative interchange of an ion-paired oxalate species for an aqua ligand is proposed to occur in the second step as a direct consequence of ligand isomerization. This mechanism successfully explains differences in the nature of the activation parameters for oxalate anation of oxalato complexes and other complexes of chromium(III). It also generalizes to provide a water exchange mechanism for oxalato complexes of chromium(III) which does not limit the anation rate.

Introduction

The mechanism of substitution of an oxalate ion¹ for aqua ligands bonded to chromium(III) has been a frequent subject of investigation during the past 3 decades. During this time a variety of investigators have determined the kinetics parameters for the reaction of Cr(H₂O)₆³⁺ with oxalic acid² and the hydrogen oxalate ion,³⁻⁵ the reaction of Cr(NH₃)₅(H₂O)³⁺ with the hydrogen oxalate and oxalate ions,⁶ the reaction of Cr(en)(H₂O)₄³⁺ with the hydrogen oxalate ion,⁷ the reaction of Cr(ox)(H₂O)₄⁺ with the hydrogen oxalate ion,^{3-5,8} and the reaction of *cis*-Cr(ox)₂(H₂O)₂⁻ with oxalic acid,⁹ the hydrogen oxalate ion,^{4,5,10} and the oxalate ion.¹⁰

Two general mechanistic features have emerged as a result of these studies. First, substitution of a bidentate oxalato-*O,O'* ligand occurs in a single observable step. Monodentate substitution of an oxalato-*O* ligand seems to be rate determining for the overall process; and chelation of the oxalato-*O* ligand must occur in a relatively rapid, associative, aqua ligand displacement step. The results of studies of the rate of oxalate substitution on Cr(NH₃)₅(H₂O)³⁺⁶ and the rate of chelation of the monodentate oxalato-*O* ligand of the transient Cr(NH₃)₅(-OCOCO)₂⁺ and Cr(NH₃)₅(-OCOCO₂H)₂⁺ reaction intermediates¹¹ strongly support this particular choice of reaction sequence. Second, ion-ion or ion-molecule association precedes the rate-determining ligand interchange step. Ion-pairing equilibrium constants have been determined from the rate data for the reaction of the hydrogen oxalate and oxalate ions with Cr(NH₃)₅(H₂O)³⁺⁶ and *cis*-Cr(ox)₂(H₂O)₂⁻,¹⁰ and association preequilibria are generally assumed to precede the rate-determining step of the other anation reactions as well.

When all similarities in the oxalate substitution reactions of this series are considered, one might reasonably conclude

that kinetic parameters would be similar for all systems or would at least exhibit a reasonable trend based upon the charge of the particular chromium(III) complex undergoing substitution. These expectations are not completely realized. Oxalate substitution rates exceed the rate of water exchange of Cr(H₂O)₆³⁺,^{12,13} Cr(NH₃)₅(H₂O)³⁺,¹⁴ and *cis*-Cr(ox)₂(H₂O)₂⁻,^{15,16} in a manner indicative of an associative interchange (I_a) substitution mechanism. However, activation enthalpies and entropies for oxalate substitution decrease as the charge of the complex ion decreases. These trends indicate an increase in associative character of the substitution reaction as the Coulombic interaction between the complex ion and the associated oxalate species is decreasing in strength. Clearly the opposite trend would be more reasonable.

It is quite possible that the composition of the coordination sphere of the parent complex is the source of the contradictory relationship between charge and reaction character. In this series, complex ions which have a formal charge lower than +3 contain one or two oxalato-*O,O'* ligands, and an oxalato ligand may activate an alternate substitution mechanism which has associative character. Data exist to support this possibility. Kallen⁹ has suggested the involvement of an oxalato-*O,O'* ligand in the oxalate anation reaction of *cis*-Cr(ox)₂(H₂O)₂⁻ to explain the similarity which exists between trans-*cis* isomerization rates and anation rates of this complex ion. Schenk and Kelm⁵ have also shown that the volumes of activation for oxalate anation of the oxalato complexes, Cr(ox)(H₂O)₄⁺ and *cis*-Cr(ox)₂(H₂O)₂⁻, differ drastically from the volume of activation of the oxalate anation reaction of Cr(H₂O)₆³⁺. However, it is difficult to base a strong mechanistic hypothesis on these data alone.

We have examined the kinetics of the oxalate anation reaction of *cis*-Cr(ox)(en)(H₂O)₂⁺ to gain additional data which

Table I. Variation of the First and Second Acid Dissociation Constants of $\text{cis-Cr}(\text{C}_2\text{O}_4)(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)(\text{H}_2\text{O})_2^+$ with Temperature in Potassium Nitrate Media

$T, ^\circ\text{C}$	I, M	$\text{p}K_{a1}^{a,b}$	$\text{p}K_{a2}^{c,d}$
10.0	1.00	6.10	8.38
20.0	0.80	5.98	8.42
25.0	0.80	5.92	8.37
25.0	1.00	5.96	8.30
30.0	0.80	5.88	8.30
35.0	0.80	5.84	8.26
40.0	0.80	5.80	8.20

^a Equilibrium: $\text{cis-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+ \rightleftharpoons \text{H}^+ + \text{Cr}(\text{ox})(\text{en})(\text{OH})(\text{H}_2\text{O})$. ^b $\Delta H = 3.7 \pm 0.2 \text{ kcal mol}^{-1}$, $\Delta S = -14.9 \pm 0.5 \text{ cal mol}^{-1} \text{ K}^{-1}$. ^c Equilibrium: $\text{Cr}(\text{ox})(\text{en})(\text{OH})(\text{H}_2\text{O}) \rightleftharpoons \text{H}^+ + \text{Cr}(\text{ox})(\text{en})(\text{OH})_2^-$. ^d $\Delta H = 4.6 \pm 0.2 \text{ kcal mol}^{-1}$, $\Delta S = -22.8 \pm 0.6 \text{ cal mol}^{-1} \text{ K}^{-1}$.

would support or reject the hypothesis that a unique substitution mechanism exists in the presence of an oxalato ligand. In this paper we report our experimental results and suggest a general mechanism to correlate the kinetics parameters for the oxalate anation and water exchange reactions of the oxalato complexes of chromium(III).

Experimental Section

The $\text{cis-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$ complex ion was isolated as its bromide salt by the method of Werner.¹⁷ This salt was reprecipitated once from water and was washed extensively with acetone to remove all traces of oxalic and hydrobromic acid. The air-dried complex salt must be stored in the dark at reduced pressure to minimize solid-state reactions which tend to produce insoluble polymeric materials. Anal. Calcd for $[\text{Cr}(\text{C}_2\text{O}_4)(\text{C}_2\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2]\text{Br}\cdot\text{H}_2\text{O}$: Cr, 15.56; N, 8.39; Br, 23.92. Found: Cr, 15.47 ± 0.02 ; N, 8.36 ± 0.02 ; Br, 23.97 ± 0.05 . Chromium and nitrogen determinations have been described elsewhere.¹⁸ Bromide was determined gravimetrically as silver bromide.

The visible absorption spectrum of solutions of the complex salt was identical with that of the $\text{Cr}(\text{ox})_2(\text{en})^-$ aquation intermediate isolated chromatographically by Kallen.¹⁸ The complex ion has visible absorption maxima at 392 nm ($\epsilon 62.2 \pm 0.2 \text{ M}^{-1} \text{ cm}^{-1}$) and 524 nm ($\epsilon 62.4 \pm 0.2 \text{ M}^{-1} \text{ cm}^{-1}$) at 25 $^\circ\text{C}$.

The acid dissociation equilibrium constants of the aqua ligands of $\text{cis-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$ were determined by potentiometric titration of $4.00 \times 10^{-2} \text{ M}$ solutions of the complex ion with 0.1000 N sodium hydroxide. Potassium nitrate was used to adjust the ionic strength of the complex ion solution and titrant to the desired values. $\text{p}K_{a1}$ and $\text{p}K_{a2}$ were evaluated as the pH of the one-quarter and three-quarter points in the titration. When the titrations were done rapidly and care was taken to exclude carbon dioxide, the half-point and end point of the titration represented a consumption of base equivalent to 1.002 \pm 0.002 and 1.997 \pm 0.002 protons, respectively. Values of $\text{p}K_{a1}$ and $\text{p}K_{a2}$ are given in Table I for temperatures between 10 and 40 $^\circ\text{C}$.

Spectrophotometric rate determinations were made at 394 nm with a Gilford Model 240 spectrophotometer served by a Lauda K2/R circulating water bath. Temperature was checked at the start of each set of three kinetics runs and was maintained at the specified value to within $\pm 0.05 \text{ }^\circ\text{C}$. Reactions were initiated by injecting 5.00 mL of a freshly prepared $\text{Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2\text{Br}\cdot\text{H}_2\text{O}$ solution into 20.00 mL of a solution containing potassium nitrate, potassium oxalate, and sufficient nitric acid to establish the desired pH,¹⁹ total oxalate concentration, ionic strength, and a complex ion concentration of $5.00 \times 10^{-3} \text{ M}$. A portion of this solution was transferred into a 1-cm cuvette in the spectrophotometer constant-temperature block within 1 min and absorbance readings were begun within 1.5 min. The cuvettes and all solutions were equilibrated at the reaction temperature prior to the start of the reaction. Each reported rate constant is the average of duplicate determinations and is precise to within $\pm 3\%$.

The absorbance increase accompanying anation of $\text{cis-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$ was followed by an extremely slow absorbance decrease and it was not possible to establish an "infinite time" absorbance value to apply to a conventional first-order data evaluation method. However, we were able to use a linear extrapolation technique to eliminate the effects of the absorbance decrease from our raw rate data. First the initial absorbance change was used to estimate the anation rate constant. Then the solution absorbance was monitored to times in excess of 10 half-lives of the reaction based on this estimate.

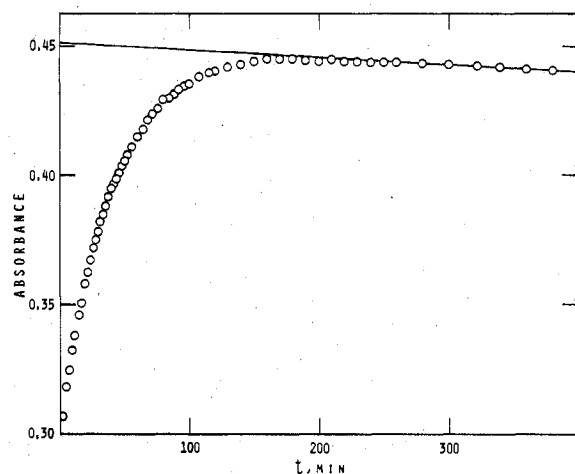


Figure 1. Absorbance data at 394 nm as a function of time for the anation of $\text{cis-Cr}(\text{C}_2\text{O}_4)(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)(\text{H}_2\text{O})_2^+$ by oxalate species. Reaction conditions: $[\text{complex}]_i = 4.83 \times 10^{-3} \text{ M}$; pH 5.00; $F_{\text{C}_2\text{O}_4} = 0.100 \text{ F}$; $I = 0.80 \text{ M}$; $T = 25.0 \text{ }^\circ\text{C}$.

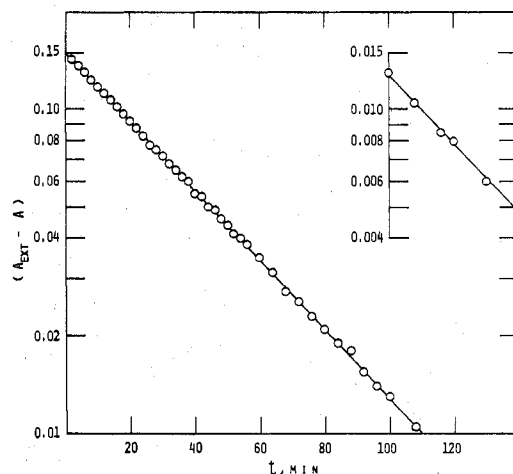


Figure 2. Semilogarithmic first-order rate plot of $(A_{\text{ext}} - A)$ vs. time for the anation of $\text{cis-Cr}(\text{C}_2\text{O}_4)(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)(\text{H}_2\text{O})_2^+$ by oxalate species. Reaction conditions: $[\text{complex}]_i = 4.83 \times 10^{-3} \text{ M}$; pH 5.00; $F_{\text{C}_2\text{O}_4} = 0.100 \text{ F}$; $I = 0.80 \text{ M}$; $T = 25.0 \text{ }^\circ\text{C}$.

The absorbance decrease after 10 half-lives was used to establish a linear absorbance extrapolation to time zero of the reaction. Finally, the anation rate constant was determined as $-2.303m$, where m is the slope of a semilogarithmic plot of the extrapolated absorbance minus the measured absorbance at each time point, $(A_{\text{ext}} - A)_t$, vs. the reaction time, t . A typical plot of "A" vs. t is shown in Figure 1, while the resulting semilog plot is shown in Figure 2. The validity of this technique is shown in part by the linearity of the final first-order rate plot through 4–6 half-lives of the anation reaction.

We have also examined the reaction of $\text{cis-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$ with oxalate species at pH 5.00 and an ionic strength of 0.80 M by chromatographing reaction mixtures at 1, 2, 4, 6, and 8 half-lives of the anation reaction. Twelve and one-half milliliters of a solution 0.0614 F in the complex ion and 0.25 F in potassium oxalate was reacted for specified times at 35.0 $^\circ\text{C}$. The reaction was then quenched by swirling the flask in an ice bath and the solution was passed through a column of Dowex 1-X8 (100–200 mesh) chloride form resin at 2 $^\circ\text{C}$. The anion exchange column effluent and washings were then passed through a column of Dowex 50-X8 (50–100 mesh) potassium form resin at 2 $^\circ\text{C}$. The effluent and washings from the cation-exchange column were assumed to contain only $\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$. The anion-exchange column retained $\text{Cr}(\text{ox})_2(\text{en})^-$ and $\text{Cr}(\text{ox})_3^{3-}$ which were eluted separately with 0.1 M KCl and 6.0 M HCl, respectively. The cation-exchange column retained only $\text{Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$ which was stripped with 0.01 M NaOH. Finally, the chromium content of each fraction was determined spectrophotometrically as CrO_4^{2-} at 373 nm ($\epsilon 4815 \text{ M}^{-1} \text{ cm}^{-1}$) after alkaline oxidation with hydrogen peroxide.²⁰ The distribution of complex species at various reaction

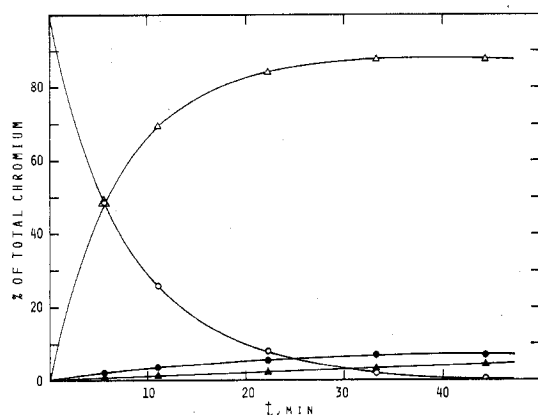


Figure 3. Species abundance at various points in the reaction of $cis\text{-Cr}(\text{C}_2\text{O}_4)(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)(\text{H}_2\text{O})_2^+$ with oxalate species. Reaction conditions: $[\text{complex}]_i = 0.0614 \text{ M}$; $\text{pH } 5.00$; $F_{\text{C}_2\text{O}_4} = 0.250 \text{ F}$; $I = 0.80 \text{ M}$; $T = 35.0 \text{ }^\circ\text{C}$. Legend: (O) $cis\text{-Cr}(\text{C}_2\text{O}_4)(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)(\text{H}_2\text{O})_2^+$; (Δ) $\text{Cr}(\text{C}_2\text{O}_4)_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)^+$; (\bullet) $\text{Cr}(\text{C}_2\text{O}_4)_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3)(\text{H}_2\text{O})$; (\blacktriangle) $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$.

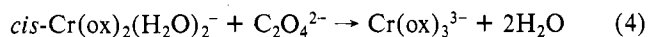
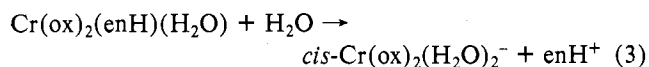
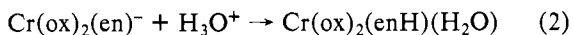
times is depicted in Figure 3 as fractions of the analytic chromium concentration vs. time. Species identity was verified by comparison of their visible absorption spectra with those reported by Kallen.¹⁸ We found no fraction which corresponded to $cis\text{-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$. If this complex was present, it existed at concentrations lower than $\text{Cr}(\text{ox})_3^{3-}$ and was eluted with $\text{Cr}(\text{ox})_2(\text{en})^-$.

Results

We have not been able to isolate $trans\text{-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$ in solution or as a salt. Therefore, designation of Werner's complex as the $cis\text{-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$ complex cannot be considered absolute. However, the major features of the complex ion's visible absorption spectrum strongly suggest that it is the cis isomer. The actual wavelength of its low-energy absorption maximum corresponds closely to the wavelength predicted for a cis complex by the rule of average environment,¹⁸ and the magnitude of molar absorptivities at the visible absorption maxima of the complex are consistent with the low-symmetry cis arrangement.²¹ Therefore we have referred to the complex as $cis\text{-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$ throughout this paper. The complex is a major product of the low-pH thermal aquation of $\text{Cr}(\text{ox})_2(\text{en})^-$,¹⁸ the sole product of photoinduced aquation of $\text{Cr}(\text{en})_2(\text{ox})^+$,²² and a major product of the anation of $\text{Cr}(\text{en})(\text{H}_2\text{O})_4^{3+}$ by oxalate species in acidic solution.⁷ No evidence exists to support the formation of appreciable quantities of a second stable isomer by any of these processes.

The results of our chromatographic study of the reaction of $cis\text{-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$ with oxalate species at pH 5 and $35.0 \text{ }^\circ\text{C}$ show that the early absorbance increase upon which we have based our kinetics study is a consequence of the anation reaction of eq 1. The slow absorbance decrease $cis\text{-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+ + \text{C}_2\text{O}_4^{2-} \rightarrow \text{Cr}(\text{ox})_2(\text{en})^- + 2\text{H}_2\text{O}$ (1)

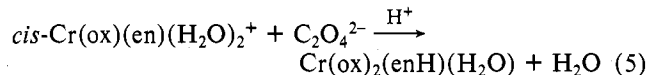
observed late in the reaction is consistent with the consecutive steps described in eq 2-4: $\text{Cr}(\text{ox})_2(\text{en})^-$ is known to aquate



in two steps to produce $cis\text{-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$;¹⁸ the equilibrium constant for formation of $\text{Cr}(\text{ox})_3^{3-}$ favors the ultimate production of this complex;²³ and each step leads to an absorbance decrease relative to $\text{Cr}(\text{ox})_2(\text{en})^-$ at 394 nm .²⁴ The fact that the rate constant of process 4 is at least a factor of 6 larger than that of process 3 under our conditions accounts for our

failure to isolate $cis\text{-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ from product mixtures at $\text{pH } 5.00$.²⁵

The distribution of species at the five sampling points of our chromatographic study is not consistent with eq 1-4 in one respect. The rate of accumulation of $\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$ and $\text{Cr}(\text{ox})_3^{3-}$ is greater than the rate projected on the basis of consecutive reactions and known rate constants. This inconsistency is resolved if $4 \pm 1\%$ of the $cis\text{-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$ reacts via the parallel pathway of eq 5 at $\text{pH } 5.00$. Oxa-



late-induced ethylenediamine aquation has been observed in other instances. One end of an ethylenediamine ligand is displaced 40% of the time when $\text{Cr}(\text{en})(\text{H}_2\text{O})_4^{3+}$ is anated by oxalate species at a hydrogen ion concentration of 0.33 M .⁷ Also, protonation of an oxalate ligand of $\text{Cr}(\text{ox})_2(\text{en})^-$ leads to partial aquation of ethylenediamine through first-order hydrogen ion dependent pathways 20% of the time.¹⁸

In the context of eq 1-5, the rate law for the anation process must correspond to eq 6 when the oxalate formality, $F_{\text{C}_2\text{O}_4}$, is

$$-k_{\text{obsd}}[cis\text{-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+] \quad (6)$$

much greater than the concentration of $cis\text{-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$ and the solution is self-buffered. The observed pseudo-first-order rate constant, k_{obsd} , must contain terms for both processes 1 and 5. We have determined values of k_{obsd} at five temperatures between 20.0 and $40.0 \text{ }^\circ\text{C}$ in two major series of rate determinations at an ionic strength of 0.80 M . First the effect of variations in $F_{\text{C}_2\text{O}_4}$ on k_{obsd} was determined at $\text{pH } 5.00$. Then the pH dependence of k_{obsd} was determined at $F_{\text{C}_2\text{O}_4} = 0.100 \text{ F}$. The effect of $F_{\text{C}_2\text{O}_4}$ and pH on the reaction rate was also determined at $25.0 \text{ }^\circ\text{C}$ and an ionic strength of 1.00 M . Potassium nitrate was used to maintain the desired ionic strength in all cases. Values of the observed rate constant for all rate determinations are given in Table II.

The dependence of k_{obsd} upon the formal oxalate concentration at $\text{pH } 5.00$ is accurately described by eq 7 at each

$$k_{\text{obsd}} = kKF_{\text{C}_2\text{O}_4}/(1 + KF_{\text{C}_2\text{O}_4}) \quad (7)$$

temperature and ionic strength. Values of k and K determined from the slope ($1/k$) and intercept ($1/kK$) plots of $F_{\text{C}_2\text{O}_4}/k_{\text{obsd}}$ vs. $F_{\text{C}_2\text{O}_4}$ at $\text{pH } 5.00$ were $k = (4.19 \pm 0.09) \times 10^{-3} \text{ s}^{-1}$ and $K = 3.97 \pm 0.14 \text{ M}^{-1}$ at $35.0 \text{ }^\circ\text{C}$, the temperature of the chromatographic study. Rate constants at other pH values indicate a complex pH dependence to the reaction rate.

The anation step of the chromatographic study must obey the integrated second-order rate law of eq 8 to be consistent

$$\frac{1}{F_{\text{C}_2\text{O}_4} - F_{\text{Cr}}} \ln \left[\frac{F_{\text{Cr}}(F_{\text{C}_2\text{O}_4} - \sum[\text{products}])}{F_{\text{C}_2\text{O}_4}(F_{\text{Cr}} - \sum[\text{products}])} \right] = kKt/(1 + 3.97F_{\text{C}_2\text{O}_4}) \quad (8)$$

with our rate data at $\text{pH } 5.00$ and $35.0 \text{ }^\circ\text{C}$. Here F_{Cr} represents the initial formality of $cis\text{-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$, $\sum[\text{products}]$ is the concentration sum of $\text{Cr}(\text{ox})_2(\text{en})^-$, $\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$, and $\text{Cr}(\text{ox})_3^{3-}$, and $F_{\text{C}_2\text{O}_4}$ is the average oxalate formality over the time interval from $t = 0$ to the sampling time, t . The chromatographic data specify $kK = (1.70 \pm 0.05) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ over five data points. This result is in excellent agreement with the value $kK = (1.66 \pm 0.09) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ specified by the kinetics data and proves that our method of treating the raw rate data successfully isolates rate constants for the anation process.

Discussion

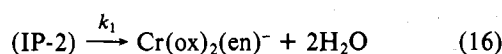
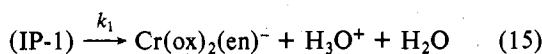
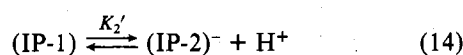
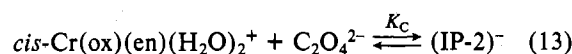
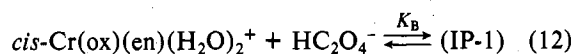
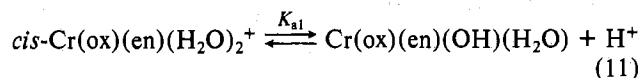
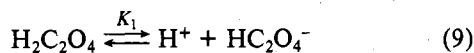
The ligand interchange mechanism proposed by Kelm and Harris¹⁰ for the anation of $cis\text{-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ by oxalate

Table II. Variation of the Observed Anation Rate Constant with Formal Oxalate Concentration, pH, Ionic Strength, and Temperature in Potassium Nitrate Media

$F_{\text{C}_2\text{O}_4}$, mol L ⁻¹	pH ^a	$10^4 k_{\text{obsd}}$, s ⁻¹	$F_{\text{C}_2\text{O}_4}$, mol L ⁻¹	pH ^a	$10^4 k_{\text{obsd}}$, s ⁻¹
(a) 20.0 °C, $I = 0.80$ M			(d) 30.0 °C, $I = 0.80$ M		
0.050	5.00	1.34	0.050	5.00	4.22
0.100	5.00	2.25	0.100	5.00	7.18
0.100	4.00	2.11	0.100	4.00	6.51
0.100	3.00	1.30	0.100	3.00	3.96
0.100	2.50	1.01	0.100	2.50	3.29
0.100	2.00	0.878	0.100	2.00	2.82
0.150	5.00	3.02	0.150	5.00	9.65
0.200	5.00	3.71	0.200	5.00	11.3
0.250	5.00	4.15	0.250	5.00	12.8
(b) 25.0 °C, $I = 0.80$ M			(e) 35.0 °C, $I = 0.80$ M		
0.050	5.00	2.31	0.050	5.00	6.95
0.100	5.00	4.10	0.100	5.00	11.8
0.100	4.50	4.03	0.100	4.00	11.0
0.100	4.00	3.76	0.100	3.00	6.78
0.100	3.50	3.12	0.100	2.50	5.68
0.100	3.00	2.35	0.100	2.00	4.84
0.100	2.52	1.89	0.150	5.00	15.8
0.100	2.50	1.88	0.200	5.00	18.6
0.100	2.00	1.61	0.250	5.00	20.8
0.150	5.00	5.32	(f) 40.0 °C, $I = 0.80$ M		
0.200	5.00	6.34	0.050	5.00	11.5
0.250	5.00	7.06	0.100	5.00	19.8
(c) 25.0 °C, $I = 1.00$ M			0.100	4.00	18.2
0.050	5.00	2.36	0.100	3.00	11.4
0.100	5.00	4.12	0.100	2.50	9.55
0.100	4.00	3.83	0.100	2.00	8.25
0.100	3.00	2.34	0.150	5.00	25.9
0.100	2.50	1.98	0.200	5.00	31.0
0.100	2.00	1.72	0.250	5.00	34.3
0.150	5.00	5.48			
0.200	5.00	6.39			
0.300	5.00	7.92			

^a Values cited are initial pH values. Oxalate ion consumption will decrease the solution pH at pH 2.00, pH 2.50, pH 3.00, and pH 3.50 by a maximum of 0.10 units, 0.16 units, 0.12 units, and 0.06 units, respectively. Solution pH should decrease by less than 0.03 pH units in solutions of initial pH ≥ 4.00 .

species generalizes extremely well to the anation reaction of $\text{cis-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$. This mechanism, summarized by eq 9–16, requires association of $\text{cis-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$ with



HC_2O_4^- and $\text{C}_2\text{O}_4^{2-}$ to form the ion pairs (IP-1) and (IP-2)⁻ prior to the rate-determining interchange of the oxalate ion and an aqua ligand. It is probable that ligand interchange occurs in an associative step (I_a). In the case of cis-Cr -

Table III. Kinetics Parameters Derived for the Anation of $\text{cis-Cr}(\text{C}_2\text{O}_4)(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)(\text{H}_2\text{O})_2^+$ by Oxalate Species^a

T , °C	$10^3 k_1$, ^d s ⁻¹	$10^4 K_2'$, ^e M ⁻¹	K_B , ^f M ⁻¹	K_C , ^g M ⁻¹
20.0 ^b	0.901 ± 0.044	7.10 ± 0.36	1.16	3.95 ± 0.17
25.0 ^b	1.44 ± 0.05	7.25 ± 0.15	1.35	4.70 ± 0.08
25.0 ^c	1.48 ± 0.03	6.42 ± 0.14	1.43	4.38 ± 0.08
30.0 ^b	2.61 ± 0.06	6.98 ± 0.09	1.31	4.36 ± 0.05
35.0 ^b	4.19 ± 0.09	6.96 ± 0.18	1.41	4.69 ± 0.11
40.0 ^b	6.85 ± 0.13	6.71 ± 0.09	1.48	4.75 ± 0.06

^a Parameters of fit to eq 17; $K_B = K_2 K_C / K_2'$. ^b $I = 0.80$ M (KNO_3). ^c $I = 1.00$ M (KNO_3). ^d $\Delta H^\ddagger = 18.1 \pm 0.4$ kcal mol⁻¹, $\Delta S^\ddagger = -10.7 \pm 1.4$ cal mol⁻¹ K⁻¹ at $I = 0.80$ M. ^e $\Delta H = -0.6 \pm 0.2$ kcal mol⁻¹, $\Delta S = -16.3 \pm 0.7$ cal mol⁻¹ K⁻¹ at $I = 0.80$ M. ^f $\Delta H = 1.9 \pm 0.5$ kcal mol⁻¹, $\Delta S = 7.0 \pm 1.6$ cal mol⁻¹ K⁻¹ at $I = 0.80$ M. ^g $\Delta H = 1.4 \pm 0.7$ kcal mol⁻¹, $\Delta S = 7.4 \pm 2.3$ cal mol⁻¹ K⁻¹ at $I = 0.80$ M.

$(\text{ox})_2(\text{H}_2\text{O})_2^-$, k_1 exceeds the water exchange rate constant by a factor of 40 and an I_a mechanism is clearly appropriate.^{15,16} It would be necessary for $\text{cis-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$ to exchange its aqua ligands 200 times faster than $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ to marginally obey the criteria for a dissociative interchange mechanism (I_d). An increase in lability of this magnitude is not reasonable considering the minor differences in complex type.

The observed rate constant derived for the I_a mechanism is given in simplest form by eq 17. This equation reduces to

$$k_{\text{obsd}} = \frac{k_1 K_C [\text{H}^+] ([\text{H}^+] + K_2') [\text{C}_2\text{O}_4^{2-}]}{K_2' ([\text{H}^+] + K_{a1}) + K_C [\text{H}^+] ([\text{H}^+] + K_2') [\text{C}_2\text{O}_4^{2-}]} \quad (17)$$

the form of eq 7 where $k = k_1$ and K is the complex conditional constant, $K = K_B K_1 [\text{H}^+] ([\text{H}^+] + K_2') / ([\text{H}^+] + K_{a1}) ([\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2)$. Therefore the ligand interchange rate constant, k_1 , may be directly determined as the reciprocal of the slope of plots of $F_{\text{C}_2\text{O}_4} / k_{\text{obsd}}$ vs. $F_{\text{C}_2\text{O}_4}$ at any fixed pH. Values of k_1 determined in this manner from data at pH 5.00 are given in Table III. The temperature dependence of k_1 between 20.0 and 40.0 °C specifies an activation enthalpy of 18.1 ± 0.4 kcal mol⁻¹ and an activation entropy of -10.7 ± 1.4 cal mol⁻¹ K⁻¹. The ligand interchange rate constant also has the same value at ionic strengths of 0.80 and 1.00 M. Ionic strength independence and a negative activation entropy are completely in accord with the requirements of an associative ligand interchange step.

Once k_1 has been determined, eq 17 may be rearranged to eq 18 to provide a means of evaluating K_2' and K_C by the $k_{\text{obsd}} ([\text{H}^+] + K_{a1}) / (k_1 - k_{\text{obsd}}) [\text{H}^+] [\text{C}_2\text{O}_4^{2-}] = (K_C / K_2') [\text{H}^+] + K_C$ (18)

method of least squares. We have used the pH-dependence data, values of k_1 determined at pH 5.00 and values of K_{a1} from Table I to evaluate K_2' and K_C from the slope (K_C / K_2') and intercept (K_C) of plots of $k_{\text{obsd}} ([\text{H}^+] + K_{a1}) / (k_1 - k_{\text{obsd}}) [\text{H}^+] [\text{C}_2\text{O}_4^{2-}]$ vs. $[\text{H}^+]$. Values of K_2' , K_B , and K_C and their standard deviations are given in Table III. Similar evaluations of the pH dependence which consider $\text{Cr}(\text{ox})(\text{en})(\text{OH})(\text{H}_2\text{O})$ as an equally active species show significant deviations from linearity. We therefore conclude that the hydroxo complex undergoes oxalate anation at a much slower rate than $\text{cis-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$.

A direct comparison of K_B and K_C with ion-pairing equilibrium constants determined for other oxalate anation reactions is not sufficient to confirm the presence of ion-pairing equilibria in our system. Determined values of K_B and K_C are approximately the same as those for $\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$,²⁶ $\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$,⁶ and $\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{OH})^{2+}$ ²⁷ despite major differences in the charge of the complex ion. In contrast

Table IV. Calculated and Observed Equilibrium Constants for the Formation of Ion Pairs between $cis\text{-Cr}(\text{C}_2\text{O}_4)(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)(\text{H}_2\text{O})_2^+$ and HC_2O_4^- or $\text{C}_2\text{O}_4^{2-}$ at 25.0 °C.

	K_B, M^{-1}	K_C, M^{-1}
calcd, $I = 0.00 \text{ M}^a$	2.32 ± 0.32	21.5 ± 6.9
calcd, $I = 0.80 \text{ M}^b$	1.12 ± 0.16	5.0 ± 1.6
obsd, $I = 0.80 \text{ M}$	1.35 ± 0.08	4.70 ± 0.08
calcd, $I = 1.00 \text{ M}^b$	1.16 ± 0.16	5.3 ± 1.7
obsd, $I = 1.00 \text{ M}$	1.43 ± 0.08	4.38 ± 0.08

^a Calculated using eq 19 and 20, $a = 4.65 \pm 0.08 \text{ \AA}$ and $\mu = 10 \pm 2 \text{ D}$. ^b Calculated using eq 19–23, $a = 4.65 \pm 0.08 \text{ \AA}$ and $\mu = 10 \pm 2 \text{ D}$.

K_B and K_C are an order of magnitude smaller than values determined for $\alpha\text{-cis-Co}(\text{EDDA})(\text{H}_2\text{O})_2^+$ ion-pairing equilibria²⁸ where charge relationships are identical. When the variability of K_B and K_C from one system to the next is considered, a theoretical approach to justification of the ion-pairing process seems to be the best alternative.

In principle the Fuoss equation²⁹ (eq 19) may be used to

$$K_{\text{IP}} = \frac{4\pi Na^3}{3000} \exp\{-U(a)/kT\} \quad (19)$$

estimate ion-pairing equilibrium constants at infinite dilution, K_{IP} . When the complex ion is not spherically symmetric, the potential energy function of the Fuoss equation, $U(a)$, must contain an ion-dipole interaction energy term in addition to the basic Coulombic energy term³⁰ (eq 20). It should be noted

$$U(a) = \frac{z+z_-e^2}{Da} + \frac{z-\mu e}{Da^2} \quad (20)$$

that $U(a)$ will reach a minimum in our system when the ion-paired oxalate species is opposite to and in the same plane as the oxalate ligand of $cis\text{-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$. Finally, we have used the Davies equation to adapt the Fuoss equation to calculation of the observable ion-pairing constant, K_{IP} , at finite ionic strength (eq 21–23).

$$K_{\text{IP}} = K_{\text{IP}}\gamma_+ \gamma_- / \gamma_{\text{IP}} \quad (21)$$

$$K_{\text{IP}} = K_{\text{IP}} \exp\left\{ \frac{z+z_-e^2\kappa}{DkT} \left[\frac{I^{1/2}}{1+I^{1/2}} - 0.2I \right] \right\} \quad (22)$$

$$\kappa = (8\pi Ne^2/1000DkT)^{1/2} \quad (23)$$

Reasonable estimates of the distance of closest approach of the associated ions, a , and the dipole moment of the complex ion, μ , are necessary for application of eq 19–23 to our system. We have estimated the distance of closest approach by applying the Fuoss equation to data for ion-pair formation between the oxalate ion and the spherically symmetric $\text{Co}(\text{NH}_3)_6^{3+}$ ion at 25 °C and infinite dilution.³¹ If K_{IP} for this

system is assumed to have an uncertainty of $\pm 10\%$, then $a = 4.65 \pm 0.08 \text{ \AA}$. The complex ion dipole moment may be calculated as $\mu = 11.0 \pm 2.2 \text{ D}$ from the experimental data at 25 °C when $a = 4.65 \text{ \AA}$. Chatt and Wilkins' study of square-planar $cis\text{-Pt}(\text{R}_3\text{P})_2\text{X}_2$ complexes³² suggests assignment of a similar dipole moment of 10 D to $cis\text{-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$. Finally, estimates of K_B and K_C given in Table IV correspond closely to our experimental values at 25 °C when $a = 4.65 \pm 0.08 \text{ \AA}$ and $\mu = 10 \pm 2 \text{ D}$. We therefore conclude that K_B and K_C reasonably describe ion-pairing equilibria which precede the rate-determining step of the anation process.

The rate constants and activation parameters of the rate-determining ligand interchange step offer no new insights into the activation process for the anation reaction when taken by themselves. However, when they are placed in the context of the oxalate anation reactions of other chromium(III) complex ions, a striking dichotomy is revealed. Generalization of the data of Table V reveals that oxalate anation reactions of chromium(III) complex species which lack an oxalato ligand proceed with a relatively high activation enthalpy and a positive activation entropy. Oxalate anation reactions of oxalato complexes of chromium(III) proceed with a relatively low activation enthalpy and a negative activation entropy. Measurements of the volume of activation also indicate a difference between oxalato complexes and other complexes of chromium(III). The activation process for the anation of $\text{Cr}(\text{ox})(\text{H}_2\text{O})_4^+$ and $cis\text{-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ by the hydrogen oxalate ion proceeds with large negative volume changes of $-8.2 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$ and $-10.0 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$, respectively.⁵ In contrast, anation of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ by the hydrogen oxalate ion has an activation volume of only $-2.2 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$. It is tempting to ascribe these differences to a transition from a dissociative to an associative interchange mechanism for the rate-determining step. However, anation rates exceed the rate of water exchange of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$,^{12,13} $\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$,¹⁴ and $cis\text{-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ ^{15,16} and probably exceed the water exchange rate of $\text{Cr}(\text{ox})(\text{H}_2\text{O})_4^+$ as well. In the latter case anation⁴ is more rapid than ¹⁸O exchange of oxalate oxygen³³ which presumably occurs without appreciable water exchange. Therefore each ligand interchange step is probably associative in character.

A qualitative understanding of the source of negative activation volumes must be considered essential to development of an appropriate anation mechanism. These data bear most directly on the negative activation entropies characteristic of the oxalate anation reactions of oxalato complexes. Large negative activation volumes have been measured for the superficially unrelated trans-cis isomerization reaction of $cis\text{-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ ($\Delta V^\ddagger = -16.6 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$)³⁴ and the racemization reactions of $\text{Cr}(\text{o-phen})(\text{ox})_2^-$, $\text{Cr}(\text{bpy})(\text{ox})_2^-$, and $\text{Cr}(\text{ox})_3^{3-}$ ($\Delta V^\ddagger = -12.3 \pm 0.3$, -12.0 ± 0.3 , and $-16.3 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$).³⁵ In these cases negative activation volumes have been attributed to an electrostrictive effect of $-10 \text{ cm}^3 \text{ mol}^{-1}$

Table V. Activation Parameters for Water Exchange and Oxalate Anation Reactions of Chromium(III) Complexes

aqua ligand exchange process	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , cal mol ⁻¹ K ⁻¹	ΔV^\ddagger , cm ³ mol ⁻¹	ref
$\text{Cr}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{C}_2\text{O}_4$	29.0	14.1		2
+ HC_2O_4^-	26.6	7.4	-2.2^a	4
+ $^{18}\text{OH}_2$	26.2	0.3	-9.3^b	13
$\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+} + \text{HC}_2\text{O}_4^-$, $\text{C}_2\text{O}_4^{2-}$	26.4	8.6		6
+ $^{18}\text{OH}_2$	23.2	0.0		14
$\text{Cr}(\text{en})(\text{H}_2\text{O})_4^{3+} + \text{HC}_2\text{O}_4^-$	23.4	7.4		7
$\text{Cr}(\text{ox})(\text{H}_2\text{O})_4^+ + \text{HC}_2\text{O}_4^-$	23.2	-0.6	-8.2^a	4
$cis\text{-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+ + \text{HC}_2\text{O}_4^-$, $\text{C}_2\text{O}_4^{2-}$	18.1	-10.7		c
$cis\text{-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^- + \text{H}_2\text{C}_2\text{O}_4$	20.7	-1.9		9
+ HC_2O_4^- , $\text{C}_2\text{O}_4^{2-}$	21.7	-10.0	-10.0^a	4
+ $^{17}\text{OH}_2$	18.0 ^d	-21.6 ^d		16

^a Reference 5. ^b Reference 36. ^c This study. ^d Computed from raw ¹⁷O exchange data.

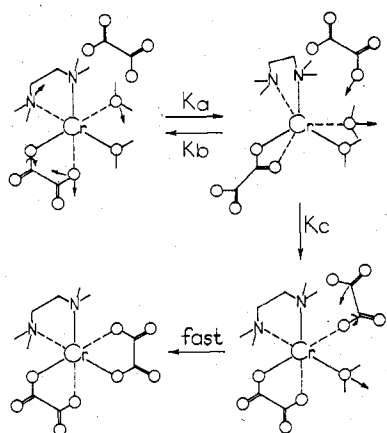


Figure 4. One-ended oxalate dissociation/associative interchange mechanism for oxalate anation of $\text{cis-Cr}(\text{C}_2\text{O}_4)(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)(\text{H}_2\text{O})_2^+$.

caused by a carboxylate group released to the surrounding solvent during one-ended dissociation of an oxalato- O,O' ligand.^{3,4,5} Isomerization and racemization also bear the relatively small activation enthalpies and negative activation entropies characteristic of oxalate anation reactions of oxalato complexes of chromium(III), and the isomerization rate of $\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ appears to limit the rate of anation of $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ by oxalate species.⁹ A reasonable explanation of the similarities in activation volume, enthalpy, and entropy exists if one-ended dissociation of an existing oxalato- O,O' ligand initiates the anation process as well as the isomerization and racemization processes.

It is unlikely that an associated oxalate or hydrogen oxalate ion would undergo substitution in concert with a simple oxalato ligand dissociation step since the ion-pairing process will preferentially locate it in a position opposite the oxalato ligand. Therefore we prefer to describe anation in terms of a two-step activation process with associative ligand interchange occurring in the second step. Details of such an activation process are shown in Figure 4 for the $\text{cis-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$ complex and may be simply extended to other oxalato complexes of chromium(III) as well.

We propose that dissociation of one end of an oxalato- O,O' ligand leads to coordination isomerization of the ligand to the oxalato- O,O configuration in the first step of the activation process (k_a). Bond formation and a partial twist of the primary coordination sphere act to stabilize the oxalato- O,O bonding configuration relative to the conventional half-bonded oxalato- O activated complex, and a large decrease in entropy and system volume must accompany the ordering of solvent molecules about the released ionic carboxylate group. We have depicted the twist as a trigonal or Bailar twist, but deviations from perfect symmetry induced by the acute O-Cr-O bond angle would give the figure the appearance of a trigonal bipyramid if the oxalato- O,O ligand is viewed as occupying one in-plane site.

In the second step of the activation process (k_c) collapse of an ionic site of the associated oxalate species is induced by the attraction of the partially exposed, positive chromium(III) center and in turn contributes to the release of an aqua ligand. When the entering oxalate species and departing aqua ligand reach a point of equal potential energy with respect to the chromium(III) center, activation of the anation process is complete. This step must compete with a dissociative reversion of the metastable oxalato- O,O ligand to the oxalato- O,O' bonding configuration (k_b).

The rate constant for the ligand interchange step, written in terms of the rate constants of Figure 4, is given by $k_1 = k_a k_c / (k_b + k_c)$. Therefore the relative magnitudes of the

kinetic parameters of k_b and k_c will determine the extent to which the activation parameters for the overall process resemble those for k_a . When $k_c > k_b$, the process parameters will be identical with those for the first step since $k_1 \approx k_a$. When $k_c < k_b$, however, $k_1 \approx k_a k_c / k_b$ and the process activation parameters will be represented by $\Delta X_1^* \approx \Delta X_a^* - \Delta X_b^* + \Delta X_c^*$ where $X = G, H, S, \text{ or } V$. Dissociation of the stabilized oxalato- O,O intermediate (k_b) should proceed with a modest activation enthalpy and a small positive entropy and volume of activation. If ligand interchange (k_c) is associative in character, it should also proceed with a modest activation enthalpy due to reductions in the Cr-OH_2 bond strength induced by the partial twist. Despite the associative nature of the interchange step, system entropy and volume may actually increase as solvent molecules are partially released by the collapsing ionic site. This point is amply illustrated by the difference in activation entropy and activation volume for water exchange³⁶ and oxalate anation⁴ of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. Therefore it is not unreasonable, even in this extreme case, that the activation parameters for anation resemble those for other processes which are initiated by one-ended dissociation of an oxalato- O,O' ligand.

The second step of this mechanism should not discriminate between associated hydrogen oxalate and oxalate ions. A single ionic site will undergo collapse in either case and kinetic parameters should be virtually the same for both species. This mechanistic point is consistent with the observation that the ligand interchange steps of $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^{10}$ and $\text{cis-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$ may be described by single rate constants whether the associated species is the hydrogen oxalate ion or the oxalate ion.

Differences in the ligand interchange rates of $\text{cis-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$, $\text{Cr}(\text{ox})(\text{H}_2\text{O})_4^+$,⁴ and $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^{10}$ are also consistent with this mechanism. The associative assist to ligand interchange via step k_c should be greater and reaction rates are greater for the monovalent species. The fact that anation of $\text{cis-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$ is more rapid than anation of $\text{Cr}(\text{ox})(\text{H}_2\text{O})_4^+$ may indicate that flexing of the ethylenediamine ligand stabilizes the partial twist proposed to exist in the oxalato- O,O intermediate's coordination sphere.

Water exchange of aqua oxalato complexes of chromium(III) may proceed by an analogous two-step mechanism in the absence of an ion-paired oxalate species. If the second step ligand interchange reaction remains associative in character, the overall activation enthalpy will again be similar to that for one-ended dissociation of an oxalato- O,O' ligand. However collapse of an associated water molecule in the second step would generate a decrease rather than an increase in activation entropy and volume. This decrease would be reflected in a water exchange rate which is slower than the anation rate. $^{17}\text{OH}_2$ exchange parameters for $\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ calculated from the data of Stieger et al.¹⁶ are consistent with this mechanistic detail.

The apparent function of the two-step one-ended oxalate dissociation/associative interchange mechanism is to provide a low-enthalpy pathway for anation despite unfavorable entropy changes which accompany its first step. In this sense it is a low-temperature mechanism and may be superseded at high temperatures by the more conventional associative mechanism which controls the substitution rates of complexes that lack an oxalato ligand. Nevertheless in the region of biological interest, one-ended dissociation of an oxalato- O,O' ligand appears to be the dominant activating step of the anation and water exchange reactions of oxalato complexes of chromium(III).

Registry No. $\text{cis-Cr}(\text{ox})(\text{en})(\text{H}_2\text{O})_2^+$, 69401-31-6; $\text{Cr}(\text{ox})(\text{en})(\text{OH})(\text{H}_2\text{O})$, 14832-08-7; $\text{Cr}(\text{ox})(\text{en})(\text{OH})_2^-$, 69351-95-7; $\text{Cr}(\text{ox})_2(\text{en})^-$, 21827-84-9; $\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})$, 56377-01-6; $\text{Cr}(\text{ox})_3^{3-}$,

15054-01-0; $C_2O_4^{2-}$, 338-70-5; $HC_2O_4^-$, 920-52-5.

References and Notes

- (1) Abbreviations used in this paper are as follows: ox = $C_2O_4^{2-}$; en = $NH_2CH_2CH_2NH_2$; enH = $-NH_2CH_2CH_2NH_3^+$; bpy = 2,2'-bipyridine; o-phen = 1,10-phenanthroline.
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- (24) Pertinent molar absorptivities at 394 nm: $Cr(ox)(en)(H_2O)_2^+$, 62.2 M⁻¹ cm⁻¹; $Cr(ox)_2(en)^-$, 100.0 M⁻¹ cm⁻¹; $Cr(ox)_2(enH)(H_2O)$, 66.6 M⁻¹ cm⁻¹; and $Cr(ox)_3^{3-}$, 83.2 M⁻¹ cm⁻¹.
- (25) $k(3) \approx k(2) = 5 \times 10^{-5}$ s⁻¹ at 35.0 °C,¹⁸ while $k(4) = 3.0 \times 10^{-4}$ s⁻¹ at 35.0 °C and an oxalate formality of 0.250 F.¹⁰
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Monomer-Dimer Phenomena in Oxoosmium(VI) Complexes

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Both monomeric and dimeric forms of the oxoosmium(VI) complexes formed by reaction between oxoosmium(VI) species and *N,N,N',N'*-tetramethylethylenediamine have been isolated and characterized by elemental analysis, by IR, UV, and NMR spectroscopy, and by molecular weight determinations. Equilibrium constants have been measured as a function of temperature. The rate of the dimer to monomer conversion has been measured as a function of pH. Corresponding 1,10-phenanthroline complexes have also been isolated and partially characterized largely through study of their IR spectra since, in this case, the equilibrium and solubility characteristics make studies in solution difficult.

Wintrebert¹ prepared an oxoosmium(VI) complex by reaction of potassium nitrite with potassium osmate or with osmium tetroxide. The complex was originally formulated as the pentacoordinate monomeric species $K_2[OsO_3(NO_2)_2]$. Atovmyan and D'yachenko² established by X-ray crystallography that the structure was, in fact, the hexacoordinate dioxo-bridged dimer $K_4[Os_2O_6(NO_2)_4]$. Criegee³ prepared a related nonionic complex by reaction between osmium tetroxide and pyridine in the presence of a reducing agent which he formulated as $OsO_3(py)_2$. Griffith and Rossetti⁴ found good spectroscopic evidence to show that this complex was also dimeric in the solid state. Solution studies⁵ suggested the existence of a monomer-dimer equilibrium for the pyridine complex, but contrary evidence has also appeared.⁶ We and others have been particularly interested in oxoosmium(VI) complexes with tertiary amines as ligands because of their synthetic utility in preparing oxoosmium(VI) esters of biologically important molecules⁷ and because of the ease with which their properties can be altered by variation in the structure of the ligand.⁸

We show in this paper that the *N,N,N',N'*-tetramethylethylenediamine (TMEN) and 1,10-phenanthroline (phen) oxoosmium(VI) complexes can be isolated in the solid state

either as dimers or as monomers.

Results

Synthesis of the Oxoosmium(VI)-*N,N,N',N'*-Tetramethylethylenediamine Complexes. The standard preparation of osmium(VI) ligand complexes involves reduction of osmium tetroxide in alkaline solution in the presence of the ligand. When this procedure is carried out with the ligand *N,N,N',N'*-tetramethylethylenediamine, a 60% yield of green crystals of the dimeric form of the complex can be isolated. If, on the other hand, the complex is made in neutral solution, the monomeric form of the complex is the principal product. However, the best procedure we have found for preparation of the monomer is by ligand exchange with the corresponding oxoosmium(VI)-bis(pyridine) complex. The complexes differ markedly in solubility properties. Both complexes are quite soluble in water and methanol, but only the monomer is soluble in acetone, chloroform, and *tert*-butyl alcohol.

Monomer-Dimer Interconversion.²⁵ The monomer-dimer interconversion can be conveniently followed in aqueous solution by NMR techniques. If the proton NMR spectrum of the dimer is observed soon after dissolution in D₂O, pD 6, only the expected pair of singlets corresponding to the methyl and