Contribution from the Departments of Chemistry, Washington State University, Pullman, Washington 99163,
and State University of New York, College at Brockport, Brockport, New York 14420

Competitive Pathways for the Oxalate Substitution Reaction of the (Glycinato-*N,O*)bis(oxalato)chromate(III) Ion

THOMAS W. KALLEN*[1] and RANDALL E. HAMM

Received January 26, 1979

The reaction of the (glycinato-*N,O*)bis(oxalato)chromate(III) complex ion with oxalic acid has been examined in potassium nitrate, sodium nitrate, and sodium perchlorate media at an ionic strength of 1.00 M in the temperature range from 44.4 to 55.8 °C. This reaction is initiated by rapid amine terminus aquation of the glycinato-*N,O* ligand in hydrogen ion dependent and hydrogen ion independent pathways and ultimately produces an equilibrium mixture of the *cis*-diaquabis(oxalato)chromate(III) ion and the tris(oxalato)chromate(III) ion. The observed reaction branches after the first reaction step. The hydrogen ion and the nitrate ion interact with the first-step product to produce the *cis*-diaquabis(oxalato)chromate(III) ion, while oxalic acid attack results in the rapid formation of the tris(oxalato)chromate(III) ion. The rate constants of the competitive hydrogen ion dependent, nitrate ion dependent, and oxalic acid dependent pathways are in the proportion 1.7:1.0:1.0. Reaction via the parallel pathways in the second step must be more rapid than the initial aquation step. In the final reaction step, the *cis*-diaquabis(oxalato)chromate(III) product of the second-step competition reacts with oxalic acid via slow, parallel, nitrate-dependent and nitrate-independent pathways to establish the final equilibrium distribution of product species. These pathways are of equal importance when the ionic strength is maintained with potassium or sodium nitrate at 1.00 M. Kinetics data are presented to support the existence of each of the parallel reaction pathways, and a mechanism is proposed for nitrate-catalyzed anation of the *cis*-diaquabis(oxalato)chromate(III) ion. The nitrate ion is proposed to exert a major accelerating effect on the anation reaction by increasing the chelation rate of the monodentate hydrogen oxalate ligand.

Introduction

We have previously reported the kinetics parameters and mechanism for the aquation of the glycinato-*N,O* ligand of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ in acidic media.[2] The dominant reaction pathway involves amine terminus aquation in the first step and carboxylate terminus aquation of the monodentate glycine-*O* ligand in the second step. Amine terminus aquation was proposed to be specific to the first step of the aquation process as a consequence of the formation of a metastable bidentate glycine-*O,O* bonding arrangement. The sole product of the aquation reaction was found to be *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$.

The anation of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ by oxalate species has also been examined in acidic solution.[3] In this case monodentate substituion of a hydrogen oxalate ligand was found to be competitive with the rapid trans–cis isomerization reaction of $Cr(C_2O_4)_2(H_2O)_2^-$. However, complete substitution of an oxalato-*O,O′* ligand was severely limited by the chelation process.

The preceding investigations allow identification of the ordinary aquation processes of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$, as well as the oxalate anation processes of stable species related to $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$. Therefore, we have examined the reaction of this complex ion with oxalate species to determine whether unusual substitution pathways specific to the glycinato-*N,O* ligand are operative. Our results elucidate the mechanism of substitution of an oxalato-*O,O′* ligand for the glycinato-*N,O* ligand and also clarify the role of the nitrate ion in the oxalate anation reaction of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$.

Experimental Section

Preparation and characterization of $K_2Ba_3[Cr(C_2O_4)_2(NH_2CH_2CO_2)]_4\cdot 18H_2O$ and the isolation and characterization of *cis*-$Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^-$ have been described elsewhere.[2]

Stock solutions of sodium perchlorate, sodium nitrate, and potassium nitrate were standardized by quantitative cation exchange for H^+ on Dowex 50W-X8 (100–200 mesh) resin, followed by titration of the column effluent with standard sodium hydroxide. Solutions for the rate determinations were prepared by quantitative dilution of the stock solutions and solid sodium oxalate, potassium oxalate monohydrate, and oxalic acid dihydrate, as appropriate, at the temperature of use. The hydrogen ion concentration and concentrations of the oxalate species were computed by assuming $K_1 = 0.0933$ M for oxalic acid at all temperatures and $\mu = 1.00$ M.[3]

Spectrophotometric rate determinations were made at 570 nm with a Gilford Model 240 spectrophotometer and Lauda K2/R circulating water bath. Temperature in the cell block was monitored at the start and end of each set of three kinetic runs and was found to be constant within 0.1 °C. Reactions were initiated by adding 25.5 mg of $K_2Ba_3[Cr(C_2O_4)_2(NH_2CH_2CO_2)]_4\cdot 18H_2O$ to 10.0 mL of temperature-equilibrated reagent solution ($T_0 = 5.00 \times 10^{-3}$ M). This solution was then transferred to a 1-cm cuvette in the cell block within 40 s of the time of mixing, and absorbance was measured manually through 90–95% of the slow reaction. "Infinite time" absorbance measurements were made at the time estimated as 10 half-lives for the slow reaction and were checked 8–12 h later.

Ashley and Hamm's method[4] was used to derive two rate constants from the raw kinetic data. The slope of semilogarithmic plots of $(A_\infty - A)$ vs. t was evaluated at large values of the reaction time, t, to determine the rate constant for a slow absorbance increase, k_b. Then, extrapolations of $(A_\infty - A)$ at small values of the reaction time, A_e, were derived from this plot and were used to correct the rate data for the effect of the slow process. The rate constant for the rapid absorbance increase, k_a, was determined from the slope of semilogarithmic plots of $(A - A_\infty - A_e)$ vs. t. The latter portion of the first plot was linear through the third and fourth half-lives of the slow process. The second plot was curved for 3–4 min but then remained linear for at least 3 half-lives. We were unable to resolve the curvature into a third rate constant and were also unable to eliminate it by careful temperature matching of the cuvettes and the reagent solution. The direction and duration of the curvature are consistent with a very rapid process which causes an increase in absorbance. Reported values of the rate constants are the average of duplicate determinations and carry an average deviation of ±4% (k_b) to ±6% (k_a).

One-millimole samples of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$, which had been reacted in 50 mL of solution for 2 and 10 half-lives of the fast process at 49.2 °C, were chromatographed on Dowex 1-X8 (100–200 mesh) resin in the NO_3^- form. The reagent solutions were 0.1250 M in oxalic acid and 0.0250 M in sodium hydrogen oxalate to minimize ionic strength and maximize the possibility of obtaining samples of $Cr(C_2O_4)_2(O_2CCO_2H)(O_2CCH_2NH_3)^{2-}$. The reaction was quenched by quick cooling of the reaction mixture to 3 °C, and the charged chromatographic columns were operated at 3 °C. Complex species were identified by their relative R_f values and visible spectra after elution, where concentrations permitted. At 2 half-lives, small quantities of the aquation intermediate, $Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^-$, were found in addition to *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$, $Cr(C_2O_4)_3^{3-}$, and the parent complex. At 10 half-lives, only *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ and $Cr(C_2O_4)_3^{3-}$ were observed during complete elution of the reaction mixture on a 25-cm resin bed at an eluent flow rate of 1 mL/10 min. Mononegative species were eluted with 0.1

0020-1669/79/1318-2151$01.00/0 © 1979 American Chemical Society

Table I. Observed Rate Constants for the Formation of $Cr(C_2O_4)_3{}^{3-}$ from $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ in Acidic Media

T, °C	[ox], M[a]	[H$^+$], M[b]	10^3k_a, s^{-1}		10^4k_b, s^{-1}		k_c/k_d
			obsd	calcd[c]	obsd	calcd[d]	
44.4[e]	0.10	0.0606	0.90	1.04	1.22	1.22	4.00
	0.13	0.0627	0.96	1.06	1.56	1.55	3.68
	0.15	0.0640	0.96	1.07	1.75	1.76	3.54
	0.18	0.0657	1.00	1.10	2.05	2.07	2.75
49.2[e]	0.10	0.0606	1.46	1.60	2.05	2.07	4.19
	0.13	0.0627	1.54	1.63	2.58	2.62	3.21
	0.15	0.0640	1.58	1.65	3.00	2.98	3.22
	0.18	0.0657	1.57	1.68	3.53	3.51	3.01
	0.20	0.0667	1.64	1.69	3.88	3.87	2.66
	0.20	0.0977	2.02	2.14	3.51	3.58	2.51
	0.30	0.1270	2.57	2.56	4.72	4.78	1.95
	0.40	0.1520	2.98	2.92	5.69	5.82	1.56
49.2[f]	0.10	0.0606	1.41	1.60	1.94	1.94[g]	3.12
	0.13	0.0627	1.50	1.63	2.42	2.46[g]	2.71
	0.15	0.0640	1.62	1.65	2.70	2.79[g]	2.83
	0.18	0.0657	1.58	1.68	3.16	3.29[g]	2.33
	0.20	0.0667	1.66	1.69	3.56	3.62[g]	2.12
	0.20	0.0977	2.08	2.14	3.32	3.32[g]	2.23
	0.30	0.1270	2.58	2.56	4.45	4.43[g]	1.89
	0.40	0.1520	3.01	2.92	5.37	5.38[g]	1.33
49.2[h]	0.10	0.0606	1.55	1.60	1.22	1.28	2.37
	0.15	0.0640	1.69	1.65	1.79	1.82	1.68
	0.20	0.0667	1.77	1.69	2.36	2.36	1.56
	0.20	0.0977	2.10	2.14	2.09	2.06	1.69
	0.30	0.1270	2.67	2.56	2.70	2.68	1.18
	0.40	0.1520	3.07	2.92	3.16	3.21	1.01
53.0[e]	0.10	0.0606	2.03	2.20	3.03	3.05	4.49
	0.13	0.0627	2.16	2.24	3.87	3.87	3.44
	0.15	0.0640	2.14	2.26	4.36	4.40	3.08
	0.18	0.0657	2.18	2.30	5.05	5.19	2.62
	0.20	0.0667	2.27	2.32	5.76	5.72	2.42
55.8[e]	0.10	0.0606	2.74	2.78	3.99	4.08	4.20
	0.13	0.0627	2.76	2.83	5.10	5.18	3.40
	0.15	0.0640	2.87	2.87	5.71	5.89	3.14

[a] Analytic oxalate concentration. [b] Calculated by assuming $K_1 = 0.0933$ for oxalic acid.[3] [c] Calculated from the rate data for amine terminus aquation of the glycinate ligand.[2] [d] Calculated from the rate data for anation of *cis*-$Cr(C_2O_4)_2(H_2O)_2{}^-$ by oxalic acid.[3] [e] $\mu = 1.00$ M (KNO_3). [f] $\mu = 1.00$ M ($NaNO_3$). [g] $k_b = \{2.80 \times 10^{-2}[H_2C_2O_4] + (3.65 \times 10^{-4})(87.4)[H^+]^2\}/(1 + 87.4 \cdot [H^+])$; this study. [h] $\mu = 1.00$ M ($NaClO_4$).

M potassium nitrate. More highly charged species were eluted with 0.5 M potassium nitrate. The visible absorption spectrum of each of the species present during the reaction is shown in Figure 1.

Results

In the presence of oxalic acid, $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ undergoes a series of reactions which have the net effect of replacing the glycinate ligand with an oxalate ligand. Under the acidic conditions of this study, $Cr(C_2O_4)_3{}^{3-}$ is not the sole product. Rather, it exists in equilibrium with *cis*-$Cr(C_2O_4)_2(H_2O)_2{}^-$ and has a concentration specified by[3] $K_3 = [Cr(C_2O_4)_3{}^{3-}][H^+]^2/[cis\text{-}Cr(C_2O_4)_2(H_2O)_2{}^-][H_2C_2O_4] = 0.890 \pm 0.012$ M. At 570 nm, the overall reaction is accompanied by the rapid absorbance decrease and slow, following absorbance increase that would be anticipated for an aquation process which is followed by anation.

We have determined rate constants for the absorbance decrease (k_a) and increase (k_b) at analytic oxalate concentrations from 0.10 to 0.20 M, an ionic strength of 1.00 M, and temperatures of 44.4, 49.2, 53.0, and 55.8 °C. Hydrogen ion concentration was maintained within a narrow range (0.0606–0.0667 M) so the effect of oxalate species upon k_a might be determined. However, these data were extended to a hydrogen ion concentration of 0.1520 M and an analytic oxalate concentration of 0.40 M at 49.2 °C. Potassium nitrate was used to maintain the ionic strength at each temperature. Sodium nitrate and sodium perchlorate were used to maintain the ionic strength at 49.2 °C alone. Values obtained for k_a and k_b are given in Table I.

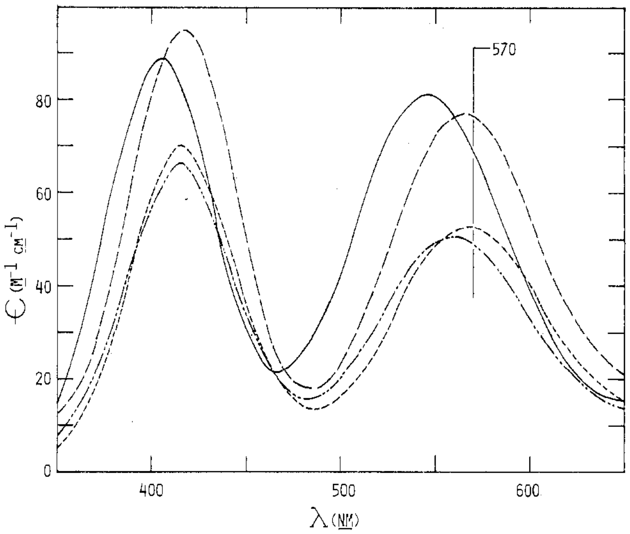

Figure 1. Visible absorption spectrum of identifiable species present during the reaction of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$ with oxalic acid: —, $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$; – – –, $Cr(C_2O_4)_3{}^{3-}$; –··–, *cis*-$Cr(C_2O_4)_2(H_2O)_2{}^-$; - - -, $Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^-$.

Pseudo-first-order rate constants for amine terminus aquation of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$, computed from extrapolations of the 20.0–34.6 °C data of Kallen and Hamm in sodium perchlorate,[2] are included in Table I. The close correspondence of k_a to these calculated rate constants identifies k_a as the pseudo-first-order rate constant for amine terminus aquation. Oxalic acid and the hydrogen oxalate ion are clearly ineffective in initiating aquation of $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$. The reaction steps and rate law for this aquation process are given in eq 1–4.[5]

$$Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-} + H_3O^+ \xrightarrow{k'} Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^- \quad (1)$$

$$Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-} + H_2O \xrightarrow{k''} Cr(C_2O_4)_2(O_2CCH_2NH_3)(OH)^{2-} \quad (2)$$

$$Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^- \overset{K_a}{\rightleftharpoons} Cr(C_2O_4)_2(O_2CCH_2NH_3)(OH)^{2-} + H^+ \quad (3)$$

$$-d \ln [Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}]/dt = k'[H^+] + k'' = k_a \quad (4)$$

Table I also contains calculated pseudo-first-order rate constants for anation of *cis*-$Cr(C_2O_4)_2(H_2O)_2{}^-$ by oxalic acid. These constants have been calculated with the use of the rate laws and rate data specific to potassium nitrate and sodium perchlorate media over the 35–55 °C temperature range.[3] The reaction steps and rate laws for the anation process are given in eq 5–9.[6] The close correspondence of k_b to the rate

$$cis\text{-}Cr(C_2O_4)_2(H_2O)_2{}^- + H_2C_2O_4 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cr(C_2O_4)_2(O_2CCO_2H)(H_2O)^{2-} + H_3O^+ \quad (5)$$

$$Cr(C_2O_4)_2(O_2CCO_2H)(H_2O)^{2-} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Cr(C_2O_4)_3{}^{3-} + H_3O^+ \quad (6)$$

$$-d \ln [cis\text{-}Cr(C_2O_4)_2(H_2O)_2{}^-]/dt = k_b \quad (7)$$

$$k_b(\text{in } KNO_3) = (k_1k_3[H_2C_2O_4] + k_2k_4[H^+]^2)/(k_3 + k_2[H^+]) \quad (8)$$

$$k_b(\text{in NaClO}_4) = k_1k_3[\text{HC}_2\text{O}_4^-]/k_2K_1 + k_4[\text{H}^+] \quad (9)$$

constants calculated for anation in potassium nitrate and sodium perchlorate media identifies k_b as the pseudo-first-order rate constant for the anation process.

While computed and observed values of k_a were in close correspondence in sodium nitrate, Kallen's rate constants for anation in potassium nitrate[3] did not adequately fit our observed values of k_b in sodium nitrate. We have fitted our data to Kallen's rate law for nitrate media (eq 8) and find $k_1 = (2.80 \pm 0.21) \times 10^{-2}$ M^{-1} s^{-1}, $k_2/k_3 = (87.4 \pm 5.9)$ M^{-1}, and $k_4 = (3.65 \pm 0.03) \times 10^{-4}$ M^{-1} s^{-1}. These values may be compared to the values $k_1 = 2.60 \times 10^{-2}$ M^{-1} s^{-1}, $k_2/k_3 = 74$ M^{-1}, and $k_4 = 4.00 \times 10^{-4}$ M^{-1} s^{-1}, calculated for potassium nitrate media at 49.2 °C. Clearly there is a small cation effect which manifests itself primarily in the ratio k_2/k_3. Within the framework of Kallen's mechanism, k_2 governs aquation of a monodentate oxalate ligand and k_3 governs its chelation rate. Values of k_b in sodium nitrate, computed with the use of our fitting parameters, are included in Table I.

We have no indication of a reaction step which has a rate constant intermediate in magnitude to k_a and k_b. Therefore, aquation of *cis*-$\text{Cr(C}_2\text{O}_4)_2(\text{O}_2\text{CCH}_2\text{NH}_3)(\text{H}_2\text{O})^-$ (eq 10), or a combination of its aquation and anation reactions (eq 10 and 11), must be more rapid than amine terminus aquation of $\text{Cr(C}_2\text{O}_4)_2(\text{NH}_2\text{CH}_2\text{CO}_2)^{2-}$. Rapid aquation is consistent with extrapolated rates for aquation of *cis*-$\text{Cr(C}_2\text{O}_4)_2(\text{O}_2\text{CCH}_3)(\text{H}_2\text{O})^{2-}$.[7] Rapid anation may explain the slight curvature of rate plots for k_a at small values of the reaction time.

$$\text{Cr(C}_2\text{O}_4)_2(\text{O}_2\text{CCH}_2\text{NH}_3)(\text{H}_2\text{O})^- \xrightarrow[\text{H}_3\text{O}^+]{k_c} cis\text{-Cr(C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^- + \text{NH}_3\text{CH}_2\text{CO}_2\text{H}^+ \quad (10)$$

$$\text{Cr(C}_2\text{O}_4)_2(\text{O}_2\text{CCH}_2\text{NH}_3)(\text{H}_2\text{O})^- \xrightarrow[\text{H}_2\text{C}_2\text{O}_4]{k_d} \text{Cr(C}_2\text{O}_4)_3^{3-} + \text{NH}_3\text{CH}_2\text{CO}_2\text{H}^+ + \text{H}_3\text{O}^+ \quad (11)$$

If pathways described by k_a, k_b, k_c, and k_d are all operative, eq 12 and 13 may be derived for the change in absorbance with time.

$$A_\infty - A = Xe^{-k_at} + Ye^{-(k_c+k_d)t} + Ze^{-k_bt} \quad (12)$$

$$Z = k_a(A_\infty - \epsilon_{\text{cis}}T_0)(k_cK_{\text{eq}} - k_d)/K_{\text{eq}}(k_a - k_b)(k_c + k_d - k_b) \quad (13)$$

Here, T_0 is the initial concentration of $\text{Cr(C}_2\text{O}_4)_2(\text{NH}_2\text{CH}_2\text{CO}_2)^{2-}$, X and Y are complex functions of rate constants and molar absorptivities, ϵ_{cis} is the molar absorptivity of *cis*-$\text{Cr(C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ (50.2 ± 0.4 M^{-1} cm^{-1} at 570 nm),[3] and $K_{\text{eq}} = K_3[\text{H}_2\text{C}_2\text{O}_4]/[\text{H}^+]^2$. When $(k_c + k_d) > k_a > k_b$, a plot of ln $(A_\infty - A)$ vs. t must become linear with a slope of $-k_b$ and "time zero" intercept equal to ln Z at large values of the reaction time.

Equation 13 may be used to verify the existence of a competitive anation pathway in the second step. Given our experimental values of Z, A_∞, T_0, k_a, and k_b, no positive value of k_c leads to a correct computed value of ϵ_{cis} when it is assumed that $k_d = 0$ or $k_c \gg k_d$. Computed values of ϵ_{cis} are invariably larger than 50.2 M^{-1} cm^{-1} and vary substantially with hydrogen ion and analytic oxalate concentrations. We therefore conclude that $\text{Cr(C}_2\text{O}_4)_2(\text{O}_2\text{CCH}_2\text{NH}_3)(\text{H}_2\text{O})^-$ undergoes aquation and anation processes at comparable rates under our set of conditions.

When $k_d \gg k_b$, eq 13 may be used to calculate the ratio k_c/k_d given experimental values of Z, A_∞, ϵ_{cis}, T_0, k_a, k_b, and K_{eq}. We have included these computed ratios in Table I for each rate determination at constant ionic strength.

Our derivation of eq 12 and 13 introduces k_c and k_d as pseudo-first-order rate constants. The following concentration-dependence fits have minimal standard deviations for the ratios of Table I: (1) $k_c/k_d = (2.9 \pm 0.3)[\text{H}^+]/[\text{H}_2\text{C}_2\text{O}_4]$ in potassium nitrate at 49.2 °C; (2) $k_c/k_d = (2.9 \pm 0.3)\cdot[\text{H}^+]/[\text{H}_2\text{C}_2\text{O}_4]$ in potassium nitrate at all temperatures; (3) $k_c/k_d = (2.4 \pm 0.3)[\text{H}^+]/[\text{H}_2\text{C}_2\text{O}_4]$ in sodium nitrate at 49.2 °C; (4) $k_c/k_d = (1.7 \pm 0.2)[\text{H}^+]/[\text{H}_2\text{C}_2\text{O}_4]$ in sodium perchlorate at 49.2 °C. The high uncertainty associated with the computation of k_c/k_d would preclude a detailed analysis of concentration dependence as a function of temperature, but it would appear that the ratio maintains the same functionality from 44.4 to 55.8 °C in potassium nitrate.

Table II. Influence of the Supporting Electrolyte on the Observed Rate Constants for Formation of $\text{Cr(C}_2\text{O}_4)_3^{3-}$ from $\text{Cr(C}_2\text{O}_4)_2(\text{NH}_2\text{CH}_2\text{CO}_2)^{2-}$ [a]

electrolyte concn, M	10^3k_a, s^{-1}			10^4k_b, s^{-1}		
	KNO$_3$ [b]	NaNO$_3$ [c]	NaClO$_4$ [c]	KNO$_3$ [b]	NaNO$_3$ [c]	NaClO$_4$ [c]
0.905	1.58	1.61	1.69	3.00	2.70	1.79
0.605	1.64	1.64	1.71	2.34	2.09	1.69
0.405	1.82	1.76	1.90	1.92	1.71	1.56
0.205	2.05	1.94	2.01	1.50	1.50	1.40
0.170		1.95			1.42	
0.105	2.20	2.06	2.19	1.24	1.34	1.28
0.000	2.45	2.45	2.45	1.10	1.20	1.20

[a] $T = 49.2$ °C, $[\text{H}_2\text{C}_2\text{O}_4] = 0.1250$ M, and $[\text{HC}_2\text{O}_4^-] = 0.0250$ M. [b] HC_2O_4^- present as its potassium salt. [c] HC_2O_4^- present as its sodium salt.

We have also determined values of k_a and k_b as a function of supporting electrolyte concentration at 49.2 °C. Oxalic acid and hydrogen oxalate formalities were maintained at 0.1250 M and 0.0250 M in all cases. Potassium and sodium nitrate and sodium perchlorate were used as the supporting electrolytes. Data for these rate determinations are given in Table II. The ratio k_c/k_d has not been computed for this set of rate determinations. The acid dissociation constant of oxalic acid, at least, is ionic-strength dependent[8] and exerts a major influence on this computation. In a qualitative sense, k_c/k_d is approximately constant in sodium perchlorate, and k_c/k_d decreases as the sodium or potassium nitrate concentration is decreased.

Values of k_a given in Table II decrease with increasing electrolyte concentration for all electrolytes. This decrease is consistent with the ionic strength behavior of the hydrogen ion dependent aquation pathway. Furthermore, these data tend to indicate minimal specific ion effects upon the amine terminus aquation rate.

Values of the anation rate constant, k_b, only exhibit a normal, nonlinear increase with electrolyte concentration in sodium perchlorate. In potassium nitrate, values of k_b show a linear increase with increases in the supporting electrolyte concentration given by $k_b = \{(2.13 \pm 0.04) \times 10^{-4}[\text{KNO}_3] + (1.06 \pm 0.02) \times 10^{-4}\}$ s^{-1}. When the supporting electrolyte is sodium nitrate, values of k_b parallel those obtained in sodium perchlorate at low concentrations and closely parallel those obtained in potassium nitrate at high concentrations. The sodium nitrate variation data may indicate a transition between the two rate laws observed by Kallen[3] in potassium nitrate (eq 8) and sodium perchlorate (eq 9) at an ionic strength of 1.00 M. If this is the case, a specific cation effect is implicated in the transition, for a similar transition does not occur when potassium nitrate is the supporting electrolyte.

Discussion

Our data specify that all reaction pathways of $\text{Cr(C}_2\text{O}_4)_2(\text{NH}_2\text{CH}_2\text{CO}_2)^{2-}$ in the presence of oxalic acid are initiated by normal amine terminus aquation of the glycinato-*N*,*O* ligand (eq 1–3). Within the limits of experimental uncertainty, this aquation step is independent of the concentration of oxalate species and the identity of the supporting electrolyte.

The reaction pathway branches after the initial aquation step. In the second observed step, *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ and $Cr(C_2O_4)_3^{3-}$ are simultaneously produced from the first-step product via competitive aquation and anation pathways. In the final reaction step, the second-step products react further to produce an equilibrium distribution of final products dominated by $Cr(C_2O_4)_3^{3-}$.

Competitive Aquation and Anation of $Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^-$. According to our data evaluation, the product of the first reaction step must undergo competitive aquation and anation processes. Two major points bear directly upon this competition. First, the ratio of aquation (k_c) and anation (k_d) rates is dependent upon the supporting electrolyte. The same rate constant ratio, k_c/k_d, is observed in potassium and sodium nitrate within the limits of experimental uncertainty. However, the rate-constant ratio is significantly smaller in sodium perchlorate. Second, the rate of anation of $Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^-$ must be competitive with a very rapid second-step aquation process.[2] As a modest estimate, the analogous $Cr(C_2O_4)_2(O_2CCH_3)(H_2O)^{2-}$ complex aquates with pseudo-first-order rate constants which are 4 times more rapid than k_a under our conditions.[7,9]

The second-step competition and its medium dependence are consistent with the reaction steps of eq 14–16. These steps

$$Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^- + H_2C_2O_4 \xrightarrow{k_d'} Cr(C_2O_4)_3^{3-} + NH_3CH_2CO_2H^+ + H_3O^+ \quad (14)$$

$$Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^- + H_3O^+ \xrightarrow{k_c'} cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- + NH_3CH_2CO_2H^+ \quad (15)$$

$$Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^- + NO_3^- + H^+ \xrightarrow{k_c''} Cr(C_2O_4)_2(NO_3)(H_2O)^{2-} + NH_3CH_2CO_2H^+ \quad (16)$$

identify the ratio of pseudo-first-order, second-step aquation and anation rate constants as $k_c/k_d = \{k_c'[H^+] + k_c''[H^+][NO_3^-]\}/(k_d'[H_2C_2O_4])$. Our data analysis in nitrate and perchlorate media would therefore specify $k_c'/k_d' = 1.7 \pm 0.2$ and $k_c''/k_d' = 1.0$ M.

We have described the nitrate-medium effect on the rate constant ratio k_c/k_d in terms of the formation of a nitrato complex in eq 16. Simple association of the supporting electrolyte anion with $Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^-$ should not be sufficient to differentiate reaction rates by itself. Association of an anion with the protonated amine group of the glycine-*O* ligand would tend to exclude water molecules from the immediate vicinity of its coordinated carboxylate terminus and decrease the rate of aquation at this site, whether the associated anion is the perchlorate ion or the nitrate ion. When the associated anion is a poor ligand, this decrease would be reflected in a net decrease in the simple displacement rate of the glycine-*O* ligand. When the associated anion is a good ligand, substitution should occur to increase the simple displacement rate. Differences in the ability of the nitrate and perchlorate ions to function as ligands[10] must therefore cause differentiation of the rate constant ratio k_c/k_d.

Rapid substitution by oxalic acid is not entirely without precedent. The rate of monodentate substitution of a hydrogen oxalate ligand on *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ is rapid when oxalic acid is the attacking species, although chelation is severely limited by an unfavorable aquation/chelation rate ratio. When the glycine-*O* ligand is the leaving group, complete substitution of an oxalato-*O,O′* ligand may be competitive with the simple aquation process. We would also note that extremely rapid oxalate exchange of $Cr(C_2O_4)_3^{3-}$ occurs under conditions analogous to ours[11,12] and may be rationalized by identical arguments.

Table III. Derived Rate Constants for the Reactions of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ with Oxalic Acid in Potassium and Sodium Nitrate Media[a]

T, °C	10^3k_1, $M^{-1}\ s^{-1}$	k_2/k_3, M^{-1}	10^5k_4, $M^{-1}\ s^{-1}$	K_3/K_1[b]
35.0[c]	4.90	128.6 ± 6.5	4.30	9.5
40.0[c]	8.12	119.7 ± 13.9	7.61	9.55
45.0[c]	13.2	115.8 ± 15.7	12.9	9.46
49.2[d]	21.0	109.2	21.8	9.41
49.2[e]	20.4	107.1 ± 10.1	21.7	9.41
49.2[f]	19.7	110.2 ± 9.4	20.4	9.41
50.0[c]	22.8	107.6 ± 8.9	24.2	9.41
55.0[c]	37.5	102.8 ± 8.5	41.4	9.43
$\Delta H^{\ddagger}$[g]	19.8 ± 0.3	−2.2 ± 0.1[h]	22.2 ± 0.4	
$\Delta S^{\ddagger}$[i]	−4.8 ± 1.1	2.4 ± 0.4[j]	−6.6 ± 1.4	

[a] $\mu = 1.00$ M. Observed rate constants are evaluated to fit $k_b = \{k_1k_3[H_2C_2O_4] + k_2k_4[H^+]\}(1 + [NO_3^-])/\{k_3(1 + [NO_3^-]) + k_2[H^+]\}$. [b] Ionic strength maintained with sodium perchlorate.[3] [c] Parameters calculated from the rate constants of ref 3; ionic strength maintained with potassium nitrate. [d] Interpolated from 35.0–55.0 °C data in potassium nitrate. [e] Parameters calculated from data in potassium nitrate; this study. [f] Parameters calculated from data in sodium nitrate; this study. [g] Units are kcal mol^{-1}. [h] The parameter cited is $\Delta H^{\ddagger}(k_2) - \Delta H^{\ddagger}(k_3)$. [i] Units are cal $mol^{-1}K^{-1}$. [j] The parameter cited is $\Delta S^{\ddagger}(k_2) - \Delta S^{\ddagger}(k_3)$.

We have proposed the existence of an aquation intermediate that contains a protonated, bidentate glycine-*O,O* ligand to rationalize the preference shown to amine terminus aquation of the glycinato-*N,O* ligand.[2] It is conceivable that the second step competition occurs at this metastable complex species rather than $Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^-$. However, the bidentate glycine-*O,O* bonding configuration must then possess sufficient kinetic stability with respect to reversion to the normal glycinato-*N,O* configuration that its further reaction is reflected in an observable second step.[13] Otherwise, the oxalic acid and supporting electrolyte dependencies that we have observed would modify the kinetics parameters of the first-step aquation process.

Anation of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$. Kallen has reported a direct nitrate dependence for the rate of anation of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ by oxalic acid when sodium nitrate is substituted for sodium perchlorate at an ionic strength of 1.00 M.[3] We have found parallel, linear increases in the anation rate with the nitrate concentration when the ionic strength is varied. Since the anation rate approaches ionic strength independence in sodium perchlorate at an ionic strength of 1.00 M, this combination of observations strongly suggests that the nitrate dependence requires a rate law term and is not simply a function of activity-coefficient variations in the various media.

We have fit Kallen's data in potassium nitrate[3] and our data in sodium nitrate at an ionic strength of 1.00 M to the form of k_b given by eq 17. First, the slope and intercept of plots

$$k_b = \frac{\{k_1k_3[H_2C_2O_4] + k_2k_4[H^+]^2\}(1 + [NO_3^-])}{k_3(1 + [NO_3^-]) + k_2[H^+]} \quad (17)$$

of $[H^+]^2/k_b$ vs. $[H^+]/(1 + [NO_3^-])$ were determined for data where $[H^+] = [HC_2O_4^-]$ by the method of least squares. This evaluation yields $(k_1/K_1 + k_2k_4/k_3)^{-1}$ as the intercept, $(k_1k_3/k_2K_1 + k_4)^{-1}$ as the slope, and k_2/k_3 as the ratio of the slope to the intercept. Kallen's method[3] was then used to derive k_1 and k_4 from the reciprocal of the slope and intercept. The results of this fitting process are given in Table III. The relative standard deviation of the slope and intercept averaged 1.4 and 7.8%, respectively. Both values are slightly lower than those obtained for fits to the simpler rate law of eq 8. In addition, eq 17 more closely represents data at constant hydrogen ion concentration which was not used in the fitting process.

Equation 17 may be generated by the reaction steps given by eq 18–23 if the appropriate assumptions are made. First,

$$cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- + NO_3^- \overset{K_A}{\rightleftharpoons} Cr(C_2O_4)_2(H_2O)(NO_3)^{2-} + H_2O \quad (18)$$

$$Cr(C_2O_4)_2(O_2CCO_2H)(H_2O)^{2-} + NO_3^- \overset{K_B}{\rightleftharpoons} Cr(C_2O_4)_2(O_2CCO_2H)(NO_3)^{3-} + H_2O \quad (19)$$

$$cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- + H_2C_2O_4 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cr(C_2O_4)_2(O_2CCO_2H)(H_2O)^{2-} + H_3O^+ \quad (20)$$

$$Cr(C_2O_4)_2(O_2CCO_2H)(H_2O)^{2-} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Cr(C_2O_4)_3^{3-} + H_3O^+ \quad (21)$$

$$Cr(C_2O_4)_2(H_2O)(NO_3)^{2-} + H_2C_2O_4 \underset{k_2'}{\overset{k_1'}{\rightleftharpoons}} Cr(C_2O_4)_2(O_2CCO_2H)(NO_3)^{3-} + H_3O^+ \quad (22)$$

$$Cr(C_2O_4)_2(O_2CCO_2H)(NO_3)^{3-} \underset{k_4'}{\overset{k_3'}{\rightleftharpoons}} Cr(C_2O_4)_3^{3-} + H^+ + NO_3^- \quad (23)$$

the steady-state condition must apply to the sum of the concentrations of $Cr(C_2O_4)_2(O_2CCO_2H)(H_2O)^{2-}$ and $Cr(C_2O_4)_2(O_2CCO_2H)(NO_3)^{3-}$. Then, K_A and K_B must represent rapidly established equilibria and have magnitudes considerably less than 1. Finally, it must be assumed that $k_1 \simeq k_1'$ and $k_4 \simeq k_4'$; i.e., nitrate is not unusually effective as a catalyst for monodentate ligand addition nor is it effective as an aquation catalyst when the complex lacks an aqua ligand. The latter assumption is supported by Guastalla and Swaddle's observations.[10]

Due to the network nature of our reaction sequence, the assumptions made for the magnitudes of k_1 and k_4 specify the equalities $k_2 = k_2'K_B/K_A$ and $k_3 = k_3'K_B$. These equalities imply that aquation rates are not affected to a large degree by the presence of the nitrato ligand and that chelation of the monodentate oxalato-*O* ligand is more rapid when nitrate is the leaving group. The former consequence is consistent with our rate ratio for competitive second-step aquation processes, k_c'/k_c'', which must have a magnitude near 1.7.

Rapid establishment of the equilibria involving the nitrato complexes (eq 18 and 19) is superficially in conflict with the slow rate known to exist for aqua ligand exchange of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$.[14,15] However, the aqua-ligand-exchange reaction has not been examined in the presence of the nitrate ion or other potentially catalytic, anionic species. If entry of the nitrate ion into the chromium(III) coordination sphere occurs with a rate constant roughly equal to k_1 for oxalic acid, the relatively high nitrate ion concentration of this study and the unfavorable aquation/chelation rate ratio for $Cr(C_2O_4)_2(O_2CCO_2H)(H_2O)^{2-}$ would work to establish eq 18 and 19 as equilibrium conditions of the system.

The parameters of Table III allow clarification of a number of mechanistic points which were not resolved by Kallen.[3] First, k_1 and k_4 show only a small dependence on the cation of the supporting electrolyte. Specific cation effects on aquation- and anation-initiating steps must be small and/or similar in magnitude. Then, the aquation rate constants in nitrate media, k_4 of Table III, are extremely close in magnitude to those estimated for sodium perchlorate media and do not differ by a factor of 2 as Kallen's data interpretation indicates.[3] Finally, the rate constant ratio k_2/k_3 is the same in potassium and sodium nitrate and is sufficiently large that the rate law will collapse to the simpler form given by eq 9 when the nitrate concentration is reduced to zero at modest hydrogen ion concentrations. This collapse successfully explains the existence of different rate laws for the anation process in nitrate and perchlorate media. Given our data at 49.2 °C in sodium nitrate, we predict a pseudo-first-order rate constant given by $k_b = \{1.92 \times 10^{-3}[HC_2O_4^-] + 2.04 \times 10^{-4}[H^+]\}\ s^{-1}$ for sodium perchlorate media when $k_2[H^+]/k_3 \gg 1$. This compares almost perfectly with the expression $k_b = \{1.91 \times 10^{-3}[HC_2O_4^-] + 2.00 \times 10^{-4}[H^+]\}\ s^{-1}$ interpolated from Kallen's data for sodium perchlorate media.[3]

Activation parameters for the rate constants of eq 17 are included in Table III. Caution must be exercised in interpretation of these parameters because they may represent the result of "averaging" similar, but not identical, nitrate-dependent and nitrate-independent pathways. Our assumptions have not taken the possible difference in temperature dependence of these pathways into consideration. Given the parameters of Table III, we estimate the activation enthalpies of k_1k_3/k_2K_1 and k_4 to be 22.0 ± 0.4 and 22.2 ± 0.4 kcal mol^{-1}, respectively, in sodium perchlorate. Observed values are 21.3 ± 0.2[3] and 21.6–22.5 kcal mol^{-1},[16,17] respectively. This close correspondence lends some credibility to, but does not prove, similar temperature dependences for the two pathways.

This system is too complex to also provide a meaningful evaluation of the role of the supporting electrolyte cation in the *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$–$Cr(C_2O_4)_3^{3-}$ equilibration mechanism or to explain the mechanism by which the nitrate ion gains rapid entry into the chromium(III) coordination sphere. In any event, the data correlation provided by eq 17 is so extensive that the proposed reaction sequence and the approximations involved in its derivation must have a high degree of validity.

Registry No. $Cr(C_2O_4)_2(NH_2CH_2CO_2)^{2-}$, 70268-34-7; $Cr(C_2O_4)_3^{3-}$, 15054-01-0; *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$, 15489-30-2; $Cr(C_2O_4)_2(O_2CCH_2NH_3)(H_2O)^-$, 61544-12-5.

References and Notes

(1) To whom correspondence should be addressed at the State University of New York.
(2) T. W. Kallen and R. E. Hamm, *Inorg. Chem.*, **16**, 1147 (1977).
(3) T. W. Kallen, *Inorg. Chem.*, **15**, 440 (1976).
(4) K. R. Ashley and R. E. Hamm, *Inorg. Chem.*, **5**, 1645 (1966).
(5) Equations 1–4 preserve the symbolism of Kallen and Hamm[2] for the amine terminus aquation process.
(6) Equations 5–9 preserve the symbolism of Kallen[3] for the anation process. K_1 is the first acid dissociation constant of oxalic acid.
(7) M. Casula, G. Illuminati, and G. Ortaggi, *Inorg. Chem.*, **11**, 1062 (1972).
(8) E. G. Moorhead and N. Sutin, *Inorg. Chem.*, **5**, 1866 (1966).
(9) We have assumed identical activation enthalpies for hydrogen ion-dependent and -independent steps in arriving at this estimate.
(10) G. Guastalla and T. W. Swaddle, *Inorg. Chem.*, **13**, 61 (1974).
(11) F. D. Graziano and G. M. Harris, *J. Phys. Chem.*, **63**, 330 (1959).
(12) D. R. Llewellyn, C. O'Connor, A. L. Odell, and R. W. Olliff, *J. Chem. Soc.*, 4627 (1964).
(13) Conversion of the glycine-*O,O* or glycine-*O* bonding arrangement to the glycinato-*N,O* bonding arrangement would be strongly inhibited by the protonated state of the amine group. The acid dissociation constant for the protonated amine group of $Co(NH_3)_5(O_2CCH_2NH_3)^{3+}$ is 3.16 × 10^{-9} M: R. Hoovwerda, E. Deutsch, and H. Taube, *Inorg. Chem.*, **11**, 1965 (1972).
(14) J. Aggett, I. Mawston, A. L. Odell, and B. E. Smith, *J. Chem. Soc. A*, 1413 (1968).
(15) H. Stieger, G. M. Harris, and H. Kelm, *Ber. Bunsenges. Phys. Chem.*, **74**, 262 (1970).
(16) D. Banerjea and M. S. Mohan, *J. Inorg. Nucl. Chem.*, **27**, 1643 (1965).
(17) H. Kelm and G. M. Harris, *Inorg. Chem.*, **6**, 1743 (1967).