

Anation of the *cis*-Diaquabis(oxalato)chromate(III) Complex Ion by Oxalate Species

THOMAS W. KALLEN\* and EDWIN J. SENKO

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The kinetics of anation of *cis*-Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> by oxalate species have been investigated in aqueous solution from 40.0 to 60.0 °C, at pH values from 3.00 to 5.00, at formal oxalate concentrations from 0.050 to 0.300 M, and at ionic strengths of 1.00, 1.20, and 1.50 M in potassium chloride, potassium nitrate, and mixed KCl/KNO<sub>3</sub> media. Observed, pseudo-first-order rate constants exhibited a complex hydrogen ion dependence and mass-law-retarded first-order dependences on both the nitrate and formal oxalate concentrations. These rate constants have been interpreted in terms of a mechanism initiated by coordination isomerization of an oxalato-*O,O'* ligand to the oxalato-*O,O* bonding mode (*k*<sub>1</sub>). Monodentate substitution at the oxalato-*O,O* intermediate competes with the reverse coordination isomerization process (*k*<sub>2</sub>) to produce *cis*-Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(OCOCO<sub>2</sub>H)(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> (*k*<sub>11</sub>) and *trans*-Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(OCOCO<sub>2</sub>H)(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> (*k*<sub>11'</sub>) when HC<sub>2</sub>O<sub>4</sub><sup>-</sup> is the attacking species. Only *cis*-Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(OCOCO<sub>2</sub>)(H<sub>2</sub>O)<sub>3</sub><sup>-</sup> is produced by C<sub>2</sub>O<sub>4</sub><sup>2-</sup> attack (*k*<sub>12</sub>). *cis*-Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(OCOCO<sub>2</sub>H)(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> and its conjugate base undergo rapid chelation to produce Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub><sup>3-</sup>, while *trans*-Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(OCOCO<sub>2</sub>H)(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> and its conjugate base aquate preferentially to *cis*-Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> in the absence of catalysis. In the presence of the nitrate ion, direct chelation of the binoxalato-*O* ligand of *trans*-Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(OCOCO<sub>2</sub>H)(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> (*k*<sub>31'</sub>) competes favorably with aquation (*k*<sub>21'</sub>) to fully activate this anation pathway. At 50.0 °C and an ionic strength of 1.20 M, *k*<sub>1</sub> = (4.02 ± 0.06) × 10<sup>-3</sup> s<sup>-1</sup>, *k*<sub>11</sub>/*k*<sub>2</sub> = 0.50 ± 0.04 M<sup>-1</sup>, *k*<sub>11'</sub>/*k*<sub>2</sub> = 0.26 ± 0.04 M<sup>-1</sup>, *k*<sub>12</sub>/*k*<sub>2</sub> = 1.56 ± 0.10 M<sup>-1</sup>, and *k*<sub>31'</sub>/*k*<sub>21'</sub> = 3.0 ± 0.5 M<sup>-1</sup>. The activation parameters of *k*<sub>1</sub> were found to be Δ*H*<sup>‡</sup> = 18.0 ± 0.2 kcal mol<sup>-1</sup> and Δ*S*<sup>‡</sup> = -14.0 ± 0.5 cal mol<sup>-1</sup> K<sup>-1</sup> at an ionic strength of 1.20 M. The reaction mechanism has been extended to include data previously reported near pH 1. The combined data show that nitrate-catalyzed anation proceeding through *trans*-Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(OCOCO<sub>2</sub>H)(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> is a process of high activation enthalpy and positive activation entropy. In contrast, substitution proceeding through *cis* intermediates has a low activation enthalpy and a negative activation entropy.

## Introduction

The nitrate ion catalyzes the oxalate anation reaction of *cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> at pH 1<sup>2,3</sup> but has not been observed to be a catalytic agent for the same reaction at pH 6.<sup>4</sup> The mechanism of nitrate-catalyzed anation has not been described in a conclusive fashion; and it is not at all clear why nitrate catalysis is not effective over a wider pH range. Furthermore, rate constants for the nitrate-dependent pathway have not been separated from those of the uncatalyzed pathway. As a consequence well-defined activation parameters are not available for either pathway. It has only been possible to state that the rate constants and activation parameters for the two pathways must be similar.<sup>3</sup>

The activation parameters of the uncatalyzed anation process are of particular interest to us. The oxalate anation reaction of *cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> has been described as having a simple associative-interchange (I<sub>a</sub>) mechanism for ligand exchange.<sup>4,5</sup> However, we feel that activation parameter correlations between this reaction system and the oxalate anation reactions of other (oxalato)chromium(III) complexes point to a special ligand-interchange step initiated by coordination isomerization of coordinated oxalate.<sup>6</sup> If this hypothesis is to be advanced, then a careful separation of activation parameters for catalyzed and uncatalyzed pathways of this and other reaction systems is essential.

We have reexamined this reaction with two goals in mind. First, we have attempted to define the mechanism of nitrate catalysis and the source of its pH dependence with more precision. Second, we have attempted to define the activation parameters for the rate-determining step of the nitrate-catalyzed and uncatalyzed oxalate anation process in an unambiguous fashion. The results of our study clarify many mechanistic points of this deceptively simple substitution reaction.

## Experimental Section

*trans*-K[Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].3H<sub>2</sub>O was prepared by Werner's method.<sup>7</sup> Anal. Calcd for K[Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].3H<sub>2</sub>O: Cr, 14.56; C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, 49.3. Found: Cr, 14.67 ± 0.02; C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, 49.4 ± 0.2.

Solutions of *cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> were prepared by ion-exchange chromatographic techniques developed elsewhere.<sup>8,9</sup> A 12.5-mmol amount of *trans*-K[Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].3H<sub>2</sub>O was allowed to isomerize for no more than 4 h in 0.2 L of water at pH 3 and 25 °C. This solution was used to charge a thermostated 25-cm<sup>3</sup> column of Dowex 1-X8 (200-400 mesh) nitrate- or chloride-form anion-exchange resin at 3 °C. The column was washed with 100 mL of 1.0 mM nitric or hydrochloric acid and was then eluted with 1.000 M potassium nitrate or potassium chloride, as appropriate. A 50-mL center cut of the band containing *cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> was collected and diluted with 1.000 M potassium nitrate or potassium chloride to attain a complex ion concentration of 25 mM (total volume 225-300 mL, yield 45-50%).

Solutions of *cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> were prepared just before their use and were stored at 3 °C. Fresh solutions were prepared weekly. Freshly prepared and properly stored solutions yield first-order anation rate plots that are linear through 90-95% of the anation reaction when the initial complex ion concentration is less than 5% of the analytic oxalate concentration. Aged solutions yield first-order anation rate plots that tend to be nonlinear after the first two half-lives, as do solutions that are contaminated by the chromatographic bands eluted before and after the *cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> fraction.

Spectrophotometric rate measurements were made at 570 nm with a Gilford Model 240 or Varian Cary 210 spectrophotometer served by a Lauda K2/R circulating thermostatic bath. Temperature was checked at the start of each set of three to five kinetics runs and was maintained to within ±0.05 °C. Cuvettes and all solutions were equilibrated at the reaction temperature prior to the start of the reaction. Reactions were initiated by injecting 5.00 mL of *cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> solution into 20.00 mL of a solution containing potassium oxalate, potassium nitrate or chloride, and sufficient nitric or hydrochloric acid to establish the desired pH,<sup>10</sup> analytic oxalate concentration, ionic strength, and a complex ion concentration of 5.00

- (1) Abbreviations used in this paper are as follows: oxH = HC<sub>2</sub>O<sub>4</sub><sup>-</sup> as the monodentate binoxalato-*O* ligand; ox = C<sub>2</sub>O<sub>4</sub><sup>2-</sup> as the bidentate oxalato-*O,O'* ligand; -ox = C<sub>2</sub>O<sub>4</sub><sup>2-</sup> as the monodentate oxalato-*O* ligand; en = NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>.
- (2) Kallen, T. W. *Inorg. Chem.* **1976**, *15*, 440.
- (3) Kallen, T. W.; Hamm, R. E. *Inorg. Chem.* **1979**, *18*, 2151.
- (4) Kelm, H.; Harris, G. M. *Inorg. Chem.* **1967**, *6*, 706.
- (5) Schenk, C.; Kelm, H. J. *Coord. Chem.* **1972**, *2*, 71.
- (6) Kallen, T. W.; Stevens, W. C.; Hammond, D. G. *Inorg. Chem.* **1979**, *18*, 1358.

(7) Werner, A. *Justus Liebigs Ann. Chem.* **1914**, *406*, 216.(8) Kallen, T. W. *Inorg. Chem.* **1975**, *14*, 2687.(9) Cr(ox)(H<sub>2</sub>O)<sub>4</sub><sup>+</sup> and Cr(ox)<sub>3</sub><sup>3-</sup> are contaminants of *cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> solutions prepared by isomerization of *trans*-K[Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].3H<sub>2</sub>O. Chromatographically prepared *cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> solutions have limited shelf lives due to continuing oxalate transfer: Stevenson, K. L.; Matson, M. S.; Patrick, R. D. J. *Inorg. Nucl. Chem.* **1971**, *33*, 147.(10) We have used the oxalic acid dissociation constants *K*<sub>1</sub> = 0.0759 M and *K*<sub>2</sub> = 2.09 × 10<sup>-4</sup> M to calculate solution composition at all temperatures of this study. These values are established at 32 °C in 1 M KNO<sub>3</sub> (Dubovenko, I. A.; Babko, I. A. *Zh. Neorg. Khim.* **1957**, *2*, 808). Computed and measured pH values agreed to within 0.02 pH unit.

**Table I.** Variation of the Observed Anation Rate Constant with Formal Oxalate Concentration, pH, Supporting Electrolyte, Ionic Strength and Temperature

<i>T</i> , °C ( <i>μ</i> , M)	<i>F</i> <sub>C<sub>2</sub>O<sub>4</sub></sub> , M <sup>b</sup>	10 <sup>4</sup> <i>k</i> <sub>obsd</sub> , s <sup>-1</sup> (KNO <sub>3</sub> ) <sup>a</sup>			10 <sup>4</sup> <i>k</i> <sub>obsd</sub> , s <sup>-1</sup> (KCl) <sup>a</sup>		
		pH 3.00 <sup>c</sup>	pH 4.00 <sup>c</sup>	pH 5.00 <sup>c</sup>	pH 3.00 <sup>c</sup>	pH 4.00 <sup>c</sup>	pH 5.00 <sup>c</sup>
60.0 (1.20)	0.050	4.61	6.60	8.32	3.49	5.78	7.69
	0.100	8.81	12.4	15.5	6.58	10.6	14.1
	0.150	12.7	17.5	21.5	9.57	15.3	19.9
	0.200	16.2	22.0	26.9	12.6	19.6	24.9
	0.250	19.4	26.2	31.0	15.1	22.9	29.3
55.0 (1.20)	0.300	22.2	29.4	35.4	17.7	26.7	33.5
	0.050	2.84	3.98	5.12	2.12	3.55	4.80
	0.100	5.48	7.54	9.55	4.09	6.68	8.82
	0.150	7.88	10.6	13.3	5.94	9.45	12.4
	0.200	10.1	13.4	16.7	7.69	12.2	15.5
50.0 (1.00)	0.250	12.0	16.2	19.4	9.33	14.4	18.2
	0.300	14.0	18.0	21.9	10.9	16.4	20.8
	0.050	1.60	2.35	2.73	1.33	2.25	2.94
	0.100	3.09	4.46	5.12	2.57	4.26	5.46
	0.150	4.44	6.33	7.17	3.74	6.07	7.68
50.0 (1.20)	0.200	5.72	8.02	9.05	4.84	7.70	9.64
	0.250	6.90	9.53	10.7	5.87	9.18	11.4
	0.300	7.99	10.9	12.2	6.84	10.6	12.9
	0.050	1.74	2.53	3.04	1.33	2.20	2.97
	0.100	3.32	4.71	5.75	2.55	4.16	5.55
50.0 (1.50)	0.150	4.78	6.72	8.04	3.70	5.94	7.86
	0.200	6.19	8.48	10.0	4.81	7.54	9.68
	0.250	7.35	10.1	11.7	5.86	8.99	11.4
	0.300	8.55	11.5	13.4	6.82	10.4	13.1
	0.050	2.03	2.98	3.65	1.59	2.85	3.63
45.0 (1.20)	0.100	3.89	5.56	6.71	3.07	5.36	6.72
	0.150	5.56	7.81	9.39	4.43	7.56	9.37
	0.200	7.11	9.86	11.7	5.71	9.54	11.8
	0.250	8.54	11.7	13.6	6.94	11.3	13.6
	0.300	9.87	13.3	15.3	8.08	12.9	15.4
40.0 (1.20)	0.050	1.04	1.52	1.82	0.787	1.32	1.78
	0.100	2.01	2.87	3.46	1.52	2.49	3.37
	0.150	2.91	4.05	4.89	2.22	3.62	4.65
	0.200	3.73	5.16	6.22	2.88	4.57	5.90
	0.250	4.50	6.19	7.21	3.52	5.46	7.05
	0.300	5.19	7.00	8.17	4.10	6.29	8.07
	0.050	0.617	0.907	1.08	0.476	0.796	1.08
	0.100	1.19	1.72	2.04	0.922	1.52	2.04
	0.150	1.72	2.45	2.90	1.35	2.18	2.90
	0.200	2.20	3.11	3.65	1.75	3.77	3.64
	0.250	2.66	3.68	4.29	2.12	3.32	4.27
	0.300	3.09	4.25	4.90	2.49	3.83	4.87

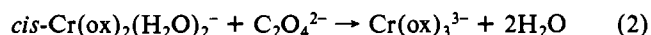
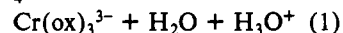
<sup>a</sup> Supporting electrolyte. <sup>b</sup> [*cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>-</sup> = 2.5 × 10<sup>-3</sup> M for *F*<sub>C<sub>2</sub>O<sub>4</sub></sub> ≤ 0.100 M. [*cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>-</sup> = 5.0 × 10<sup>-3</sup> M for *F*<sub>C<sub>2</sub>O<sub>4</sub></sub> > 0.100 M. <sup>c</sup> Values cited are initial pH values. Solution pH should decrease by less than 0.06 unit due to consumption of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> during reactions at pH 3. Solution pH should decrease by less than 0.03 unit during reactions at pH 4.00 or pH 5.00.

× 10<sup>-3</sup> M.<sup>11</sup> A portion of this solution was transferred into a 1-cm cuvette in the spectrophotometer constant-temperature block within 1 min. Absorbance measurements *A<sub>t</sub>* were begun within 1.5 min and were continued through 95% of the total absorbance change (4–5 half-lives). Infinite time absorbance measurements *A<sub>∞</sub>* were made after an equivalent, additional time interval. Pseudo-first-order rate constants *k*<sub>obsd</sub> were determined from these data as the slope of plots of -ln (*A<sub>∞</sub>* - *A<sub>t</sub>*) vs. reaction time *t*.

Most reported rate constants are the result of single rate determinations, but selected replications indicate reproducibility to within ±2%.

## Results

The overall reaction equation for the anation of *cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> by oxalate species is most closely approximated by eq 1 at pH 3 (81.8% HC<sub>2</sub>O<sub>4</sub><sup>-</sup>) and by eq 2 at pH 5 (95.4% *cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> + HC<sub>2</sub>O<sub>4</sub><sup>-</sup> →



(11) The complex ion concentration was reduced to 2.50 mM for analytic oxalate concentrations of 0.050 and 0.100 M to keep the change in oxalate concentration under 5% during the measured portion of the reaction.

C<sub>2</sub>O<sub>4</sub><sup>2-</sup>).<sup>10</sup> "Infinite time" absorption spectra of the reaction product at pH 3.00, *F*<sub>C<sub>2</sub>O<sub>4</sub></sub> = 0.0500 M, and 50.0 °C confirm that Cr(ox)<sub>3</sub><sup>3-</sup> is the sole product of the reaction in both potassium nitrate and potassium chloride media, as do the "Infinite time" absorbance measurements at 570 nm when the reaction is conducted under conditions more favorable for formation of Cr(ox)<sub>3</sub><sup>3-</sup>.<sup>12</sup> As a consequence the pseudo-first-order rate constant of the anation rate law (eq 3) should

$$d[\text{cis-Cr(ox)}_2(\text{H}_2\text{O})_2^-]/dt = -k_{\text{obsd}}[\text{cis-Cr(ox)}_2(\text{H}_2\text{O})_2^-] \quad (3)$$

contain no significant term describing aquation of Cr(ox)<sub>3</sub><sup>3-</sup>. It is also unlikely that *cis*-Cr(ox)<sub>2</sub>(OH)(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> plays a role in the anation mechanism. Considerably less than 1% of the reactant complex will be in its basic form in the pH range of this study.<sup>13</sup>

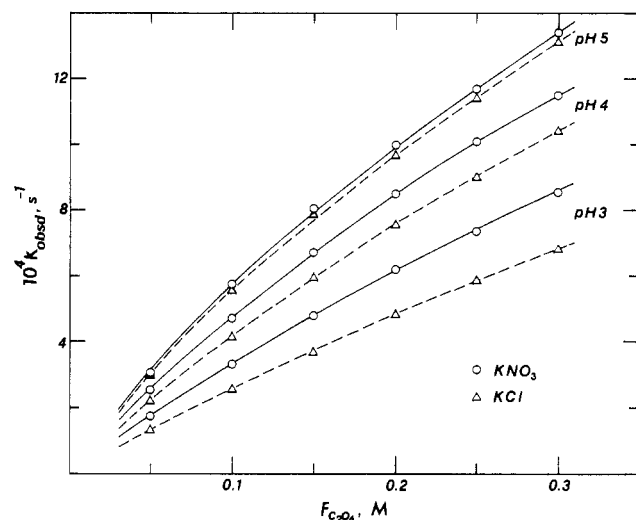
(12) Conditional formation equilibrium constants calculated from the data of ref 2 are [Cr(ox)<sub>3</sub><sup>3-</sup>]/[*cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>-</sup>*F*<sub>C<sub>2</sub>O<sub>4</sub></sub> = 9.6 × 10<sup>3</sup>, 3.8 × 10<sup>4</sup>, and 5.4 × 10<sup>4</sup> M<sup>-1</sup> at pH 3, 4, and 5, respectively. The final concentration of *cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> and aquation rate law terms should be negligible at each pH.

(13) p*K*<sub>1</sub> = 7.10 for *cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> at 25 °C and *μ* = 0.05 M: Kelm, H.; Harris, G. M. *Z. Phys. Chem. (Wiesbaden)* **1969**, *66*, 8.

**Table II.** Conditional Kinetics Parameters Derived for the Anation of  $cis\text{-Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  by Oxalate Species in Potassium Nitrate and Potassium Chloride Media<sup>a</sup>

$T, ^\circ\text{C}$ ( $\mu, \text{M}$ )	pH	$\text{KNO}_3^b$		$\text{KCl}^b$	
		$10^3 k_1, \text{s}^{-1}$	$K_c, \text{M}^{-1}$	$10^3 k_1, \text{s}^{-1}$	$K_c, \text{M}^{-1}$
60.0 (1.20)	3	9.48 ± 0.23	1.03 ± 0.03	10.1 ± 0.8	0.71 ± 0.06
	4	9.68 ± 0.23	1.47 ± 0.04	9.83 ± 0.60	1.23 ± 0.08
	5	9.93 ± 0.24	1.84 ± 0.05	10.2 ± 0.2	1.61 ± 0.04
55.0 (1.20)	3	6.26 ± 0.18	0.96 ± 0.03	6.36 ± 0.09	0.69 ± 0.01
	4	6.29 ± 0.31	1.36 ± 0.07	6.09 ± 0.21	1.24 ± 0.04
	5	6.33 ± 0.12	1.77 ± 0.04	6.25 ± 0.11	1.65 ± 0.03
50.0 (1.00)	3	3.95 ± 0.05	0.85 ± 0.01	4.01 ± 0.03	0.69 ± 0.01
	4	3.99 ± 0.04	1.26 ± 0.01	4.08 ± 0.05	1.17 ± 0.01
	5	3.98 ± 0.04	1.47 ± 0.01	4.04 ± 0.03	1.57 ± 0.01
50.0 (1.20)	3	3.95 ± 0.12	0.92 ± 0.03	4.04 ± 0.15	0.68 ± 0.03
	4	4.03 ± 0.07	1.33 ± 0.02	4.05 ± 0.06	1.15 ± 0.02
	5	4.07 ± 0.11	1.63 ± 0.05	4.01 ± 0.12	1.60 ± 0.05
50.0 (1.50)	3	4.30 ± 0.04	0.99 ± 0.01	4.38 ± 0.08	0.75 ± 0.01
	4	4.36 ± 0.05	1.46 ± 0.02	4.36 ± 0.01	1.40 ± 0.01
	5	4.26 ± 0.06	1.88 ± 0.03	4.38 ± 0.10	1.82 ± 0.05
45.0 (1.20)	3	2.57 ± 0.06	0.85 ± 0.02	2.66 ± 0.06	0.61 ± 0.01
	4	2.57 ± 0.07	1.26 ± 0.04	2.56 ± 0.08	1.08 ± 0.03
	5	2.69 ± 0.13	1.42 ± 0.07	2.72 ± 0.11	1.40 ± 0.06
40.0 (1.20)	3	1.54 ± 0.02	0.84 ± 0.01	1.61 ± 0.03	0.61 ± 0.01
	4	1.59 ± 0.03	1.21 ± 0.02	1.60 ± 0.01	1.05 ± 0.01
	5	1.66 ± 0.04	1.40 ± 0.03	1.62 ± 0.04	1.44 ± 0.04

<sup>a</sup> Derived by linear "least-squares" analysis of the function  $F_{\text{C}_2\text{O}_4}/k_{\text{obsd}} = (1/k_1)F_{\text{C}_2\text{O}_4} + (1/k_1K_c)$ . <sup>b</sup> Supporting electrolyte.



**Figure 1.** Variation of the observed, pseudo-first-order anation rate constant with formal oxalate concentration, pH, and reaction medium at 50.0 °C and  $\mu = 1.20 \text{ M}$ .

We have measured  $k_{\text{obsd}}$  at pH 3.00, 4.00, and 5.00 at each of five temperatures in the range from 40.0 to 60.0 °C. The analytic oxalate concentration,  $F_{\text{C}_2\text{O}_4}$ , was varied from 0.0500 to 0.300 M at each pH value. Potassium nitrate and potassium chloride were used to maintain the ionic strength at 1.00, 1.20, or 1.50 M in parallel series of rate determinations. Values of  $k_{\text{obsd}}$  are given in Table I for each set of conditions, while Figure 1 demonstrates the dependence of  $k_{\text{obsd}}$  upon  $F_{\text{C}_2\text{O}_4}$ , pH, and supporting electrolyte at 50.0 °C and  $\mu = 1.20 \text{ M}$ .

The functional relationship between  $k_{\text{obsd}}$  and  $F_{\text{C}_2\text{O}_4}$  is best described by eq 4 at each condition of pH, temperature, and

$$k_{\text{obsd}} = k_1 K_c F_{\text{C}_2\text{O}_4} / (1 + K_c F_{\text{C}_2\text{O}_4}) \quad (4)$$

ionic strength, despite an apparent dependence of the rate constant on the anion of the supporting electrolyte. Values of  $k_1$  and  $K_c$ , calculated from the linear least-squares slope ( $1/k_1$ ) and intercept ( $1/k_1 K_c$ ) of plots of  $F_{\text{C}_2\text{O}_4}/k_{\text{obsd}}$  vs.  $F_{\text{C}_2\text{O}_4}$ , are given in Table II for each condition of pH, temperature, and ionic strength in both supporting electrolytes.

The parameters of Table II confirm two major points deduced by Kelm and Harris<sup>4</sup> for this anation reaction: (1) the

rate constant  $k_1$  is independent of pH and supporting electrolyte, within the limits of experimental uncertainty; (2) the complete pH dependence of  $k_{\text{obsd}}$  is contained within  $K_c$ .

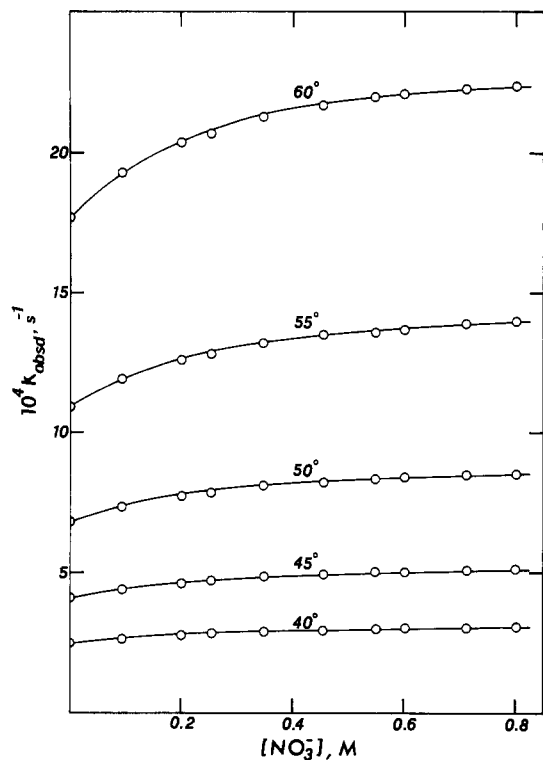
Several new and important points are also revealed by these data: (1)  $K_c$  has a small but significant temperature dependence in both media; (2)  $K_c$  is larger when potassium nitrate is used as the supporting electrolyte at a particular pH; (3) values of  $K_c$  in the two media converge as pH increases. The last result tends to rule out formation of  $\text{Cr}(\text{ox})_2(\text{NO}_3)(\text{H}_2\text{O})_2^{2-}$  or  $\text{Cr}(\text{ox})_2\text{Cl}(\text{H}_2\text{O})_2^{2-}$  as a significant feature of the reaction mechanism. The formation of these species should be independent of pH in the pH region where the conjugate bases of  $cis\text{-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$  exist at negligible concentrations. However, it is consistent with a form of nitrate catalysis that is only effective within the low-pH anation pathways; and it explains why we have observed nitrate catalysis near pH 1<sup>2,3</sup> while Kelm and Harris failed to find evidence of nitrate catalysis at pH 6.<sup>4</sup>

Our data show the rate constant  $k_1$  to increase only slightly with increases in ionic strength, while  $K_c$  has an ionic strength dependence characteristic of the interaction of  $cis\text{-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$  with  $\text{HC}_2\text{O}_4^-$  at low pH and with  $\text{C}_2\text{O}_4^{2-}$  at high pH.<sup>14</sup> These results strongly parallel those obtained for the anation of  $cis\text{-Cr}(\text{en})(\text{ox})(\text{H}_2\text{O})_2^+$  by oxalate species<sup>6</sup> and favor the assignment of  $k_1$  to a similar intramolecular rearrangement process.

Finally, we have measured  $k_{\text{obsd}}$  as a function of the nitrate concentration and temperature at pH 3.00,  $F_{\text{C}_2\text{O}_4} = 0.300 \text{ M}$ , and  $\mu = 1.20 \text{ M}$ . These values of  $k_{\text{obsd}}$  are given in Table III.

The relationship between  $k_{\text{obsd}}$  and  $[\text{NO}_3^-]$  in mixed media, illustrated in Figure 2, is typical of a pseudo-first-order rate constant having both first-order and inverse first-order nitrate dependences. The nitrate-induced acceleration of the anation reaction is small and approaches a limiting value at rather low nitrate concentrations (ca. 90% of the observed acceleration is achieved by  $[\text{NO}_3^-] = 0.6 \text{ M}$ ). As a consequence, rate constants obtained at nitrate concentrations greater than 0.6 M will fail to show an effective nitrate dependence. It must

(14) These conclusions are in conflict with the results of Kelm and Harris,<sup>4</sup> who have assigned a substantial ionic strength dependence to  $k_1$  and none at all to  $K_c$ . Their partitioning may be in error due to pH variations introduced by their method of preparing solutions.



**Figure 2.** Variation of the observed, pseudo-first-order anation rate constant with nitrate concentration and temperature at pH 3.00,  $F_{\text{C}_2\text{O}_4} = 0.300 \text{ M}$ ,  $T = 50.0 \text{ }^\circ\text{C}$ , and  $\mu = 1.20 \text{ M}$  in potassium chloride/potassium nitrate mixed media.

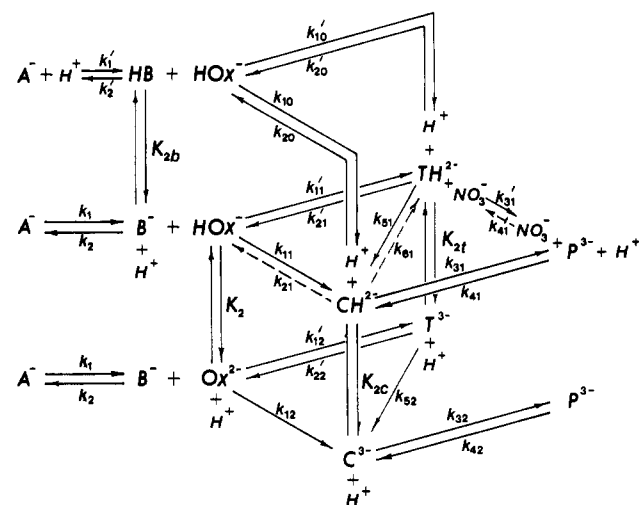
be noted that the nitrate media rate constants of Table I were measured either at nitrate concentrations greater than 0.6 M (pH 3 and 4) or at a pH where nitrate catalysis is relatively ineffective (pH 5). Therefore, the values of  $k_1$  and  $K_c$  given in Table II for nitrate media should be independent of the nitrate concentration.<sup>15</sup>

### Discussion

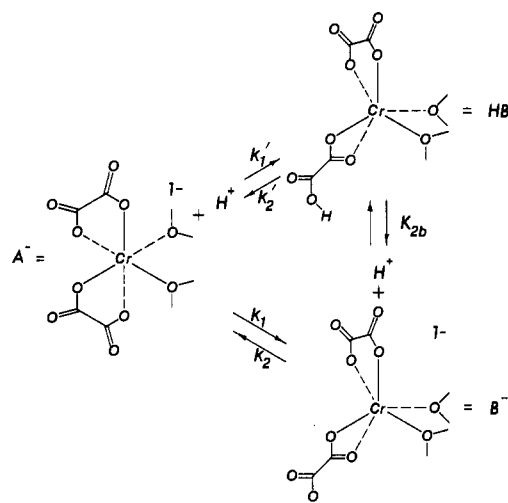
In principle our data may be interpreted by modifying the ion pair/associative-interchange mechanism of Kelm and Harris<sup>4</sup> to include a pathway for nitrate catalysis. However, our data would then require formation equilibrium constants of 0.5 and  $1.6 \text{ M}^{-1}$  for the ion pairs of  $\text{HC}_2\text{O}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$  with *cis*- $\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$  at  $50.0 \text{ }^\circ\text{C}$  and  $\mu = 1.20 \text{ M}$ . Barring ion-ion or ion-dipole interactions of a highly unusual nature, these ion-pair formation equilibrium constants should be much smaller. We estimate the constants to be 0.10 and  $0.04 \text{ M}^{-1}$  in the absence of ion-dipole interactions, or 0.14 and  $0.18 \text{ M}^{-1}$  if a dipole moment of 10 D is assigned to *cis*- $\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ .<sup>16</sup> If these estimates have only a modest degree of validity, then ion-pair formation should not be an observable feature of the substitution mechanism.

Attempts to rationalize the nitrate dependence of  $k_{\text{obsd}}$  with ion-pair formation equilibria fail for similar reasons. The formation equilibrium constant necessary to generate the observed nitrate dependence,  $3 \text{ M}^{-1}$  at  $50.0 \text{ }^\circ\text{C}$ , pH 3.00, and

### Scheme I



### Scheme II



$\mu = 1.20 \text{ M}$ , is too large to be explained by an ordinary ion-pairing interaction between *cis*- $\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$  and the nitrate ion. If this constant is assumed to describe a complexation equilibrium instead, then  $\text{Cr}(\text{ox})_2(\text{NO}_3)(\text{H}_2\text{O})_2^{2-}$  must be the dominant reactive complex at the high nitrate concentrations of our oxalate dependence study. In this case it would be extremely difficult to justify our observation that rate constants in nitrate and chloride media fit the same functional form of  $k_{\text{obsd}}$  to generate the same value for the derived rate constant  $k_1$  under all conditions of pH and formal oxalate concentration.

A variety of steady-state substitution mechanisms may be used to fit the nonlinear oxalate dependence of  $k_{\text{obsd}}$  without involving ion-pair formation equilibria. However, the point of entry of the nitrate ion into the formal substitution mechanism is much more difficult to define. The nonlinear form, limited nature,<sup>17</sup> and pH dependence of the nitrate effect combine to suggest that the nitrate ion does not initiate a new anation pathway. Instead, it may simply accelerate a preexisting but relatively ineffective, pH-dependent anation pathway to a rate limit defined by its first steps.

The substitution mechanism of Scheme I may be used to fit the data we have collected in the pH interval from pH 3 to pH 5. We have chosen this particular reaction scheme over many other possibilities for several reasons: (1) it may also be used to fit data previously collected near pH 1<sup>2,3</sup> with a high

(15) The ratio  $(k_{\text{obsd}})_{\text{KNO}_3}/(k_{\text{obsd}})_{\text{KCl}}$  fails to show a definite trend as supporting electrolyte concentration increases at a particular pH. Instead, it remains constant within the uncertainty limits of the individual rate constants ( $1.044 \pm 0.037$  at pH 5,  $1.127 \pm 0.017$  at pH 4, and  $1.294 \pm 0.029$  at pH 3). A constant ratio would be observed if both observed rate constants had exactly parallel anion dependences or if neither observed rate constant was dependent on the supporting electrolyte anion.

(16) We have estimated the ion-pair formation equilibrium constants by the method of ref 6. Our estimates are based on an interionic separation of  $4.65 \times 10^{-8} \text{ cm}$ .

(17)  $\text{Cr}(\text{H}_2\text{O})_5(\text{NO}_3)^{2+}$  has been found to be  $10^5$  more labile than  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  under the same conditions: Mitchell, M. L.; Montag, T.; Espenson, J. H.; King, E. L. *Inorg. Chem.* 1975, 14, 2862.

**Table III.** Variation of the Observed Anation Rate Constant with the Nitrate Concentration and Temperature at pH 3.00,  $F_{C_2O_4} = 0.300$  M, and  $\mu = 1.20$  M

[NO <sub>3</sub> <sup>-</sup> ], M <sup>a</sup>	10 <sup>4</sup> k <sub>obsd</sub> , s <sup>-1</sup>				
	40.0 °C	45.0 °C	50.0 °C	55.0 °C	60.0 °C
0.0000 <sup>b</sup>	2.49	4.10	6.82	10.9	17.7
0.0937 <sup>b</sup>	2.65	4.42	7.36	11.9	19.3
0.200	2.78	4.65	7.74	12.6	20.4
0.253 <sup>b</sup>	2.83	4.74	7.83	12.8	20.7
0.348 <sup>b</sup>	2.90	4.87	8.11	13.2	21.3
0.453	2.95	4.95	8.23	13.5	21.7
0.548	3.00	5.07	8.35	13.6	22.0
0.601 <sup>b</sup>	3.02	5.07	8.41	13.7	22.1
0.711	3.06	5.15	8.50	13.9	22.3
0.801	3.09	5.19	8.55	14.0	22.4
m <sup>c</sup>	-11.39 ± 0.27	-13.22 ± 0.46	-13.20 ± 0.62	-14.14 ± 0.44	-14.86 ± 0.38
b <sup>c</sup>	3.09 ± 0.06	3.66 ± 0.10	3.98 ± 0.16	4.53 ± 0.12	4.83 ± 0.11
[k <sub>11</sub> 'k <sub>31</sub> ' / (k <sub>2</sub> 'k <sub>21</sub> ')] <sub>m</sub> <sup>d</sup>	0.49 ± 0.10	0.66 ± 0.11	0.75 ± 0.13	0.90 ± 0.18	1.14 ± 0.19
[k <sub>11</sub> 'k <sub>31</sub> ' / (k <sub>2</sub> 'k <sub>21</sub> ')] <sub>b</sub> <sup>e</sup>	0.55 ± 0.11	0.74 ± 0.13	0.83 ± 0.15	1.01 ± 0.20	1.23 ± 0.21

<sup>a</sup> [NO<sub>3</sub><sup>-</sup>] + [Cl<sup>-</sup>] = 0.801 M. <sup>b</sup> *cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> was added as its solution in 1.00 M KCl. <sup>c</sup> (k<sub>obsd</sub> - k<sub>Cl</sub>)k<sub>1</sub>' / (k<sub>1</sub> - k<sub>obsd</sub>)k<sub>Cl</sub>[NO<sub>3</sub><sup>-</sup>] = mk<sub>obsd</sub>' / (k<sub>1</sub> - k<sub>obsd</sub>) + b. <sup>d</sup> Derived from the slope, m, of the function of footnote c. <sup>e</sup> Derived from the intercept, b, of the function of footnote c.

degree of internal consistency; (2) it may be used to explain the limited nature and pH dependence of nitrate catalysis in a simple fashion; (3) it introduces reactive intermediates that have a high probability of existence; (4) it leads to derived kinetic parameters that stand the test of reasonability.

Within Scheme I, substitution of HC<sub>2</sub>O<sub>4</sub><sup>-</sup> or C<sub>2</sub>O<sub>4</sub><sup>2-</sup> occurs after coordination isomerization (k<sub>1</sub>) of an oxalato-*O,O'* ligand of *cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> (A<sup>-</sup>) produces a more reactive complex containing the oxalato-*O,O* ligand (B<sup>-</sup>). The protonated form of the oxalato-*O,O* intermediate (HB) exists in equilibrium with B<sup>-</sup> and may also be produced by a hydrogen ion catalyzed pathway (k<sub>1</sub>'). Substitution competes with the reverse coordination isomerization processes (k<sub>2</sub> and k<sub>2</sub>') to limit the concentrations of the reactive intermediates HB and B<sup>-</sup> to steady-state levels. Details of the coordination isomerization processes are shown in Scheme II.

Attacked by oxalate species at different locations on the protonated or unprotonated oxalato-*O,O* intermediates will produce both *cis* (k<sub>10</sub>, k<sub>11</sub>, and k<sub>12</sub>) and *trans* (k<sub>10</sub>', k<sub>11</sub>', and k<sub>12</sub>') species containing monodentate oxalato-*O* or binoxalato-*O* ligands. The monodentate oxalato ligands of *cis*-Cr(ox)<sub>2</sub>(oxH)(H<sub>2</sub>O)<sub>2</sub><sup>2-</sup> (CH<sup>2-</sup>) and its conjugate base, *cis*-Cr(ox)<sub>2</sub>(-ox)(H<sub>2</sub>O)<sub>2</sub><sup>3-</sup> (C<sup>3-</sup>) should chelate (k<sub>31</sub> and k<sub>32</sub>) to produce Cr(ox)<sub>3</sub><sup>3-</sup> (P<sup>3-</sup>) at rapid rates by intramolecular displacement of water.<sup>18</sup> However, *trans*-Cr(ox)<sub>2</sub>(oxH)(H<sub>2</sub>O)<sub>2</sub><sup>2-</sup> (TH<sup>2-</sup>) and its conjugate base, *trans*-Cr(ox)<sub>2</sub>(-ox)(H<sub>2</sub>O)<sub>2</sub><sup>3-</sup> (T<sup>3-</sup>), must isomerize to their *cis* forms (k<sub>51</sub> and k<sub>52</sub>) before chelation will occur by this mechanism. Isomerization is not likely to compete favorably with aquation of the monodentate oxalato-*O* or binoxalato-*O* ligands (k<sub>21</sub>' and k<sub>22</sub>');<sup>19</sup> and the anation pathways involving *trans* intermediates may be completely ineffective in the absence of some form of catalysis.

Within the framework of the early reaction steps and observed concentration dependences, the nitrate ion must effect a single-step chelation of *trans*-Cr(ox)<sub>2</sub>(oxH)(H<sub>2</sub>O)<sub>2</sub><sup>2-</sup> to produce Cr(ox)<sub>3</sub><sup>3-</sup> directly (k<sub>31</sub>'). Parallel evaluations of data near pH 1 and data in the pH 3–5 interval lead to mutually contradictory conclusions if the nitrate ion is assumed to catalyze the *trans*-*cis* isomerization of Cr(ox)<sub>2</sub>(oxH)(H<sub>2</sub>O)<sub>2</sub><sup>2-</sup> instead. The Scheme I mechanism does not include a nitrate-catalyzed pathway for chelation of *trans*-Cr(ox)<sub>2</sub>(-ox)(H<sub>2</sub>O)<sub>2</sub><sup>3-</sup> because

the nitrate ion has little catalytic effect at pH 5. However, we cannot determine from our data whether the absence of effective nitrate catalysis is due to a small formation rate for *trans*-Cr(ox)<sub>2</sub>(-ox)(H<sub>2</sub>O)<sub>2</sub><sup>3-</sup> at high pH or to the inability of the nitrate ion to interact in a constructive fashion with a trinegative complex.

The overall anation reaction of Scheme I is effectively unidirectional from pH 3 to pH 5 but proceeds to an equilibrium distribution of complex species near pH 1. To simplify derived rate laws, we have evaluated the anation rate data in the pH 3–5 interval and the data near pH 1 separately, using slightly different approximations.

**Evaluation and Discussion of Anation Data from pH 3 to pH 5.** All processes involving the protonated oxalato-*O,O* intermediate, HB of Scheme I, have been neglected in our evaluation of the anation data in the pH 3–5 interval. Then, only three approximations are necessary to derive an appropriate, general rate law for the anation process: (1) *cis*-Cr(ox)<sub>2</sub>(oxH)(H<sub>2</sub>O)<sub>2</sub><sup>2-</sup> and *cis*-Cr(ox)<sub>2</sub>(-ox)(H<sub>2</sub>O)<sub>2</sub><sup>3-</sup> must undergo chelation more rapidly than they aquate to the oxalato-*O,O* intermediate or isomerize to their *trans* forms, such that they effectively exist in equilibrium with the product, Cr(ox)<sub>3</sub><sup>3-</sup>. This equilibrium must strongly favor Cr(ox)<sub>3</sub><sup>3-</sup>. (2) The sum of the concentrations of *trans*-Cr(ox)<sub>2</sub>(oxH)(H<sub>2</sub>O)<sub>2</sub><sup>2-</sup> and *trans*-Cr(ox)<sub>2</sub>(-ox)(H<sub>2</sub>O)<sub>2</sub><sup>3-</sup> must obey the steady-state condition d([TH<sup>2-</sup>] + [T<sup>3-</sup>])/dt = 0. (3) The concentration of the coordination isomer of *cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> must also obey the steady-state condition, d[B<sup>-</sup>]/dt = 0. When these approximations are valid, k<sub>obsd</sub> of the derived rate law has the form given by eq 5, where v = k<sub>11</sub>[H<sup>+</sup>] + k<sub>12</sub>K<sub>2</sub>, w = (k<sub>11</sub> +

$$k_{11}') [H^+] + (k_{12} + k_{12}') K_2, x = k_{21}' [H^+] + k_{22}' K_{21}, y = (k_{51} + k_{31}' [NO_3^-]) [H^+] + k_{52} K_{21}, \text{ and } z = [H^+]^2 + K_1 [H^+] + K_1 K_2. \quad (5)$$

Two different, approximate forms of k<sub>obsd</sub>, specific to chloride and nitrate media, result if two additional conditions are obeyed: (1) aquation of *trans* intermediates must be more rapid than isomerization in the absence of nitrate catalysis (i.e., (k<sub>21</sub>'[H<sup>+</sup>] + k<sub>22</sub>'K<sub>21</sub>) ≫ (k<sub>51</sub>[H<sup>+</sup>] + k<sub>52</sub>K<sub>21</sub>) when [NO<sub>3</sub><sup>-</sup>] = 0); (2) nitrate-catalyzed chelation of *trans*-Cr(ox)<sub>2</sub>(oxH)(H<sub>2</sub>O)<sub>2</sub><sup>2-</sup> must be more rapid than aquation of the *trans* intermediates at high nitrate concentrations (i.e., k<sub>31</sub>'[NO<sub>3</sub><sup>-</sup>][H<sup>+</sup>] ≫ (k<sub>21</sub>'[H<sup>+</sup>] + k<sub>22</sub>'K<sub>21</sub>) when [NO<sub>3</sub><sup>-</sup>] ≫ 0). Then

(18) Ramasami, T.; Wharton, R. K.; Sykes, A. G. *Inorg. Chem.* **1975**, *14*, 359.

(19) Casula, M.; Illuminati, G.; Ortaggi, G. *Inorg. Chem.* **1972**, *11*, 1062.

Table IV. Specific Kinetics Parameters for the Anation of *cis*-Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> by Oxalate Species in Potassium Nitrate and Potassium Chloride Media

	T, °C						
	40.0	45.0	50.0	50.0	50.0	55.0	60.0
μ, M	1.20	1.20	1.00	1.20	1.50	1.20	1.20
10 <sup>3</sup> k <sub>1</sub> , s <sup>-1</sup> (KNO <sub>3</sub> ) <sup>a</sup>	1.60 ± 0.06	2.61 ± 0.07	3.97 ± 0.02	4.02 ± 0.06	4.31 ± 0.05	6.29 ± 0.04	9.70 ± 0.23
10 <sup>3</sup> k <sub>1</sub> , s <sup>-1</sup> (KCl) <sup>a</sup>	1.61 ± 0.01	2.65 ± 0.08	4.04 ± 0.04	4.03 ± 0.02	4.37 ± 0.01	6.23 ± 0.14	10.0 ± 0.2
(k <sub>11</sub> + k <sub>11</sub> ')/k <sub>2</sub> , M <sup>-1</sup>	0.67 ± 0.03	0.70 ± 0.02	0.72 ± 0.01	0.76 ± 0.02	0.82 ± 0.03	0.80 ± 0.04	0.84 ± 0.04
(k <sub>12</sub> + k <sub>12</sub> ')/k <sub>2</sub> , M <sup>-1</sup>	1.48 ± 0.06	1.53 ± 0.05	1.51 ± 0.01	1.65 ± 0.05	1.85 ± 0.08	1.73 ± 0.10	1.86 ± 0.10
k <sub>11</sub> /k <sub>2</sub> , M <sup>-1</sup>	0.45 ± 0.03	0.45 ± 0.03	0.52 ± 0.03	0.50 ± 0.04	0.53 ± 0.01	0.52 ± 0.03	0.53 ± 0.03
k <sub>12</sub> /k <sub>2</sub> , M <sup>-1</sup>	1.42 ± 0.09	1.41 ± 0.09	1.56 ± 0.07	1.56 ± 0.10	1.85 ± 0.03	1.63 ± 0.09	1.62 ± 0.09
k <sub>11</sub> '/k <sub>2</sub> , M <sup>-1</sup>	0.22 ± 0.04	0.25 ± 0.04	0.20 ± 0.03	0.26 ± 0.04	0.29 ± 0.03	0.28 ± 0.05	0.31 ± 0.05
k <sub>12</sub> '/k <sub>2</sub> , M <sup>-1</sup>	0.06 ± 0.11	0.12 ± 0.10	-0.05 ± 0.07	0.09 ± 0.11	0.00 ± 0.09	0.10 ± 0.13	0.24 ± 0.13
k <sub>11</sub> 'k <sub>31</sub> '/k <sub>2</sub> k <sub>21</sub> ', M <sup>-2</sup>	0.52 ± 0.04	0.70 ± 0.06	(0.64 ± 0.06) <sup>b</sup>	0.79 ± 0.06		0.96 ± 0.08	1.18 ± 0.06
k <sub>31</sub> '/k <sub>21</sub> ', M <sup>-1</sup>	2.4 ± 0.5	2.8 ± 0.5	(3.2 ± 0.6) <sup>b</sup>	3.0 ± 0.5		3.4 ± 0.7	3.8 ± 0.6

<sup>a</sup> Supporting electrolyte. <sup>b</sup> Derived from the data of: Kallen, T. W. *Inorg. Chem.* 1976, 15, 440. Kallen, T. W.; Hamm, R. E. *Ibid.* 1979, 18, 2151.

$k_{\text{obsd}}$  will be approximated by eq 6 when [NO<sub>3</sub><sup>-</sup>] = 0 and by eq 7 when [NO<sub>3</sub><sup>-</sup>] ≫ 0.

$$(k_{\text{obsd}})_{\text{KCl}} \approx k_1 K_1 v F_{\text{C}_2\text{O}_4} / (z k_2 + K_1 v F_{\text{C}_2\text{O}_4}) \quad (6)$$

$$(k_{\text{obsd}})_{\text{KNO}_3} \approx k_1 K_1 w F_{\text{C}_2\text{O}_4} / (z k_2 + K_1 w F_{\text{C}_2\text{O}_4}) \quad (7)$$

The correspondence of eq 6 and 7 to eq 4 identifies the medium-independent and pH-invariant rate constant  $k_1$  of Table II as the rate constant for coordination isomerization of *cis*-Cr(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup>. It also specifies that  $K_c$  of eq 4 and Table II should have the functional form of eq 8 in potassium

$$(K_c)_{\text{KCl}} = (k_{11} K_1 / z k_2) [\text{H}^+] + k_{12} K_1 K_2 / z k_2 \quad (8)$$

$$(K_c)_{\text{KNO}_3} = ((k_{11} + k_{11}') K_1 / z k_2) [\text{H}^+] + (k_{12} + k_{12}') K_1 K_2 / z k_2 \quad (9)$$

chloride media and of eq 9 in potassium nitrate media. Therefore, the pH dependence of  $K_c$  in each medium may be fitted to the linear functions given by eq 10 and 11 to evaluate

$$z(K_c)_{\text{KCl}} / K_1 = (k_{11} / k_2) [\text{H}^+] + k_{12} K_2 / k_2 \quad (10)$$

$$z(K_c)_{\text{KNO}_3} / K_1 = ((k_{11} + k_{11}') / k_2) [\text{H}^+] + (k_{12} + k_{12}') K_2 / k_2 \quad (11)$$

the rate constant ratios  $k_{11}/k_2$ ,  $k_{12}/k_2$ ,  $(k_{11} + k_{11}')/k_2$ , and  $(k_{12} + k_{12}')/k_2$ , directly. Values derived for each rate constant ratio are given in Table IV.

Rate constants obtained in mixed media (Table III) were measured at nitrate concentrations where  $k_{31}'[\text{NO}_3^-][\text{H}^+] \approx (k_{21}'[\text{H}^+] + k_{22}'K_{21})$ . Therefore, the full form of  $k_{\text{obsd}}$  must be used to describe their nitrate dependence. Equation 5 may be rearranged to yield the complex linear equation described by eq 12-14, where  $k_{\text{Cl}}$  is the value of  $k_{\text{obsd}}$  when [NO<sub>3</sub><sup>-</sup>] =

$$(k_{\text{obsd}} - k_{\text{Cl}})k_1 / (k_1 - k_{\text{obsd}})k_{\text{Cl}}[\text{NO}_3^-] = m(k_{\text{obsd}} / (k_1 - k_{\text{obsd}})) + b \quad (12)$$

$$m = -(k_{11}'k_{31}' / k_2 k_{21}')k_2^2 z [\text{H}^+] / v(w - v)K_1 F_{\text{C}_2\text{O}_4} \quad (13)$$

$$b = (k_{11}'k_{31}' / k_2 k_{21}')k_2 w [\text{H}^+] / v(w - v) \quad (14)$$

0. If eq 5 is an accurate representation of  $k_{\text{obsd}}$ , then the data of Table III must provide a linear fit to eq 12 at each temperature; the same rate constant ratio,  $k_{11}'k_{31}'/k_2 k_{21}'$ , should be obtained by applying our derived rate constant ratios to the slope and intercept of the fitting equation at a particular temperature. Linear least-squares values of  $m$  and  $b$  and the values of  $k_{11}'k_{31}'/k_2 k_{21}'$  derived from  $m$  and  $b$  are included in Table III. The linear fits of data and the rate constant ratio correspondence are exceptional, considering the limited effect of the nitrate ion on  $k_{\text{obsd}}$  at pH 3. Average values of the rate constant ratios  $k_{11}'k_{31}'/k_2 k_{21}'$  and  $k_{31}'/k_{21}'$  are given in Table IV.

We have analyzed the temperature dependence of each rate constant ratio of Table IV by evaluating the linear variation

Table V. Activation Parameters for the Anation of *cis*-Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> by Oxalate Species at μ = 1.20 M

	ΔH <sup>‡</sup> ,	ΔS <sup>‡</sup> ,
	kcal mol <sup>-1</sup>	cal mol <sup>-1</sup> K <sup>-1</sup>
k <sub>1</sub> <sup>a</sup>	18.0 ± 0.2	-14.0 ± 0.5
k <sub>41</sub> <sup>b</sup>	21.6	-8.6
k <sub>41</sub> <sup>c</sup>	25.5 ± 1.1	3.9 ± 3.3
k <sub>1</sub> k <sub>11</sub> 'k <sub>31</sub> '/k <sub>2</sub> k <sub>21</sub> ' <sup>c</sup>	21.2 ± 0.2	-5.4 ± 0.5
k <sub>1</sub> k <sub>11</sub> 'k <sub>31</sub> '/k <sub>2</sub> k <sub>21</sub> '	26.1 ± 0.6	10.6 ± 1.8
	Δ(ΔH <sup>‡</sup> ),	Δ(ΔS <sup>‡</sup> ),
	kcal mol <sup>-1</sup> d	cal mol <sup>-1</sup> K <sup>-1</sup> e
k <sub>11</sub> /k <sub>2</sub>	2.0 ± 0.4	4.6 ± 1.1
k <sub>12</sub> /k <sub>2</sub>	1.6 ± 0.4	5.9 ± 1.3
k <sub>11</sub> '/k <sub>2</sub>	3.3 ± 0.3	7.6 ± 0.9
k <sub>31</sub> '/k <sub>21</sub> ' <sup>c</sup>	1.2 ± 0.5	4.0 ± 1.3
k <sub>31</sub> '/k <sub>21</sub> '	4.6 ± 0.3	16.5 ± 0.8
k <sub>11</sub> 'k <sub>31</sub> '/k <sub>2</sub> k <sub>21</sub> '	8.1 ± 0.6	24.6 ± 1.7

<sup>a</sup> For combined data in KNO<sub>3</sub> and KCl. <sup>b</sup> Calculated from the data of: Banerjee, D.; Mohan, M. S. *J. Inorg. Nucl. Chem.* 1965, 27, 1643. Kelm, H.; Harris, G. M. *Inorg. Chem.* 1967, 6, 1743. μ = 1.00 M. <sup>c</sup> Calculated from the data of: Kallen, T. W. *Inorg. Chem.* 1976, 15, 440. Kallen, T. W.; Hamm, R. E. *Ibid.* 1979, 18, 2151. μ = 1.00 M. <sup>d</sup> Δ(ΔH<sup>‡</sup>)<sub>ij</sub> = (ΔH<sup>‡</sup>)<sub>k<sub>i</sub></sub> - (ΔH<sup>‡</sup>)<sub>k<sub>j</sub></sub> for k<sub>i</sub>/k<sub>j</sub>. <sup>e</sup> Δ(ΔS<sup>‡</sup>)<sub>ij</sub> = (ΔS<sup>‡</sup>)<sub>k<sub>i</sub></sub> - (ΔS<sup>‡</sup>)<sub>k<sub>j</sub></sub> for k<sub>i</sub>/k<sub>j</sub>.

of -R ln (k<sub>i</sub>/k<sub>j</sub>) with 1/T at μ = 1.20 M. The slope of the resulting function must be equal to Δ(ΔH<sup>‡</sup>)<sub>ij</sub> = ΔH<sub>i</sub><sup>‡</sup> - ΔH<sub>j</sub><sup>‡</sup>, while the intercept is given by -Δ(ΔS<sup>‡</sup>)<sub>ij</sub> = -(ΔS<sub>i</sub><sup>‡</sup> - ΔS<sub>j</sub><sup>‡</sup>). Values of the rate constant ratios and their activation parameter differences (Table V) serve as additional tests of the Scheme I mechanism. Each must itself be "reasonable", or must lead to reasonable conclusions, within the framework of the proposed mechanism.

Relative values of the monodentate substitution/coordination isomerization rate constant ratios are consistent with the geometry shown in Scheme II for the reactive diaqua(oxalato-O,O')(oxalato-O,O)chromate(III) intermediate. This roughly trigonal intermediate should be susceptible to attack at three different sites. Attack at either of the two sites of relatively positive polarity adjacent to aqua ligands will tend to be limited to the ionic carboxylate groups of HC<sub>2</sub>O<sub>4</sub><sup>-</sup> or C<sub>2</sub>O<sub>4</sub><sup>2-</sup> and should lead to a *cis* product when water is the leaving group. Attack at the site of relatively negative polarity opposite the aqua ligands will tend to be restricted to the protonated carboxylate group of HC<sub>2</sub>O<sub>4</sub><sup>-</sup> and should lead to a *trans* product. Therefore one might expect substitution initiated by HC<sub>2</sub>O<sub>4</sub><sup>-</sup> to lead to *trans* and *cis* products in a 1:2 ratio, while substitution initiated by C<sub>2</sub>O<sub>4</sub><sup>2-</sup> should lead to a *cis* product alone. In fact, our results demonstrate that (k<sub>11</sub>'/k<sub>11</sub>) ≈ 1:2 while (k<sub>12</sub>'/k<sub>12</sub>) ≈ 0.

We would also expect the activation parameters for *cis* substitution to be the same whether HC<sub>2</sub>O<sub>4</sub><sup>-</sup> or C<sub>2</sub>O<sub>4</sub><sup>2-</sup> were

the attacking species. However, extensive rearrangement must occur to produce an activated complex having a rough trans symmetry and trans substitution initiated by  $\text{HC}_2\text{O}_4^-$  should require larger values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ . The experimental results again confirm our expectations:  $\Delta(\Delta H^\ddagger)$  and  $\Delta(\Delta S^\ddagger)$  for  $k_{11}/k_2$  and  $k_{12}/k_2$  are the same within the limits of experimental uncertainty;  $k_{11}'/k_2$  has larger values for its activation parameter differences than either  $k_{11}/k_2$  or  $k_{12}/k_2$ .

In the context of Scheme I,  $k_{31}'/k_{21}'$  describes the competition between nitrate-catalyzed chelation and uncatalyzed aquation of *trans*- $\text{Cr}(\text{ox})_2(\text{oxH})(\text{H}_2\text{O})^{2-}$ . Therefore it is not surprising that the activation parameter differences of  $k_{31}'/k_{21}'$  bear little resemblance to those of  $k_{11}/k_2$ ,  $k_{12}/k_2$ , or  $k_{11}'/k_2$ . The large values of  $\Delta(\Delta H^\ddagger)$  and  $\Delta(\Delta S^\ddagger)$  associated with  $k_{31}'/k_{21}'$  do imply that the nitrate-catalyzed chelation step must have considerable dissociative character.

While the existence of a rate-determining step prior to oxalate substitution is implied by the soundness of the preceding correlations, these correlations do not identify the first step as coordination isomerization in direct fashion. However, it is important to recognize that the product of the first step must be a metastable intermediate, not an unstable "activated complex". It is more reasonable to expect the six-coordinate oxalato-*O,O* intermediate to fulfill this condition than five-coordinate intermediates such as  $\text{Cr}(\text{ox})_2(\text{H}_2\text{O})^-$  or the diaqua(oxalato-*O,O'*)(oxalato-*O*)chromate(III) ion. The latter intermediate may in fact serve as the activated complex for coordination isomerization.

The activation parameters derived for  $k_1$ ,  $\Delta H^\ddagger = 18.0 \pm 0.2 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -14.0 \pm 0.5 \text{ cal mol}^{-1} \text{ K}^{-1}$ , resemble the activation parameters for the rate-determining step of the *cis*- $\text{Cr}(\text{en})(\text{ox})(\text{H}_2\text{O})_2^+$  oxalate anation mechanism so closely ( $\Delta H^\ddagger = 18.1 \pm 0.4 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -10.7 \pm 1.4 \text{ cal mol}^{-1} \text{ K}^{-1}$ )<sup>6</sup> that both processes must have the same activating step. The activation parameters of  $k_1$  also resemble those for water exchange of *cis*- $\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$  ( $\Delta H^\ddagger = 18.0 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -21.6 \text{ cal mol}^{-1} \text{ K}^{-1}$ )<sup>20</sup> but water exchange is slower due to its more negative activation entropy. This relationship is consistent with a water-exchange process that is also activated by coordination isomerization of an oxalato-*O,O'* ligand.<sup>6</sup> These correlations offer strong support to the general hypothesis that coordination isomerization of an oxalato-*O,O'* ligand to the oxalato-*O,O* bonding arrangement initiates the substitution mechanisms of all chromium(III) oxalato complexes.

**Evaluation and Discussion of Anation Data near pH 1.** Extension of our mechanism to fit data previously reported near pH 1<sup>2,3</sup> represents a demanding but necessary test of mechanistic details. Many otherwise reasonable alternate mechanisms fail to lead to reasonable conclusions when they are extended to include these data. All processes of Scheme I that involve  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{C}^{3-}$ , and  $\text{T}^{3-}$  have been neglected in this data evaluation.

An appropriate rate law may be derived if three conditions are obeyed: (1) the steady-state condition  $d([\text{HB}] + [\text{B}^-])/dt = 0$  must apply to the sum of the concentrations of protonated and unprotonated oxalato-*O,O* intermediates; (2) *cis*- and *trans*- $\text{Cr}(\text{ox})_2(\text{oxH})(\text{H}_2\text{O})^{2-}$  must exist in hydrogen ion catalyzed equilibrium and obey the steady-state condition  $d([\text{CH}^{2-}] + [\text{TH}^{2-}])/dt = 0$ ; (3)  $(k_{20} + k_{20}')[\text{H}^+] \gg (k_{21} + k_{21}')$ . While these conditions apply,  $k_{\text{obsd}}$  of the equilibration rate law will have the form of eq 15. Equation 15 is equivalent

$$k_{\text{obsd}} = \{((k_1 k_{11} k_{31} / k_2 k_{21}) [\text{HC}_2\text{O}_4^-] + k_{41} [\text{H}^+]) [\text{H}^+] \times (1 + (k_{41}' / k_{41}) [\text{NO}_3^-])\} / \{[\text{H}^+] + (k_{11} k_{31} K_{2b} / k_{21} (k_{10} + k_{10}')) (1 + (k_{41}' / k_{41}) [\text{NO}_3^-])\} \quad (15)$$

**Table VI.** Kinetics Parameters for the Anation of *cis*- $\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  by Oxalate Species at pH ~1

$T, ^\circ\text{C}$	$10^3 k_1 k_{11} k_{31} / (k_2 k_{21}),$	$10^4 k_{41},$	$10^4 k_{41}',$	$10^3 k_{11} k_{31} K_{2b} / [k_{21} (k_{10} + k_{10}')],$
	$\text{M}^{-1} \text{s}^{-1} a, d$	$\text{M}^{-1} \text{s}^{-1} b, d$	$\text{M}^{-2} \text{s}^{-1} d, e$	$\text{M}^{-1} a, e$
55.0	3.49 ± 0.01	3.7	4.7 ± 0.1	8.9 ± 0.7
50.0	2.07 ± 0.04	2.2	2.7 ± 0.1	8.6 ± 0.6
49.2	1.89 ± 0.05 <sup>c, d</sup>	2.0	2.1 ± 0.1 <sup>c, e</sup>	9.0 ± 0.7 <sup>c, e</sup>
49.2		2.0	2.4 ± 0.1 <sup>c, f</sup>	8.9 ± 0.7 <sup>c, f</sup>
45.0	1.23 ± 0.01	1.3	1.3 ± 0.1	8.7 ± 1.0
40.0	0.697 ± 0.009	0.73	0.70 ± 0.08	7.4 ± 2.0

<sup>a</sup> Calculated from the data of: Kallen, T. W. *Inorg. Chem.* 1976, 15, 440. <sup>b</sup> Calculated from the data of: Banerjee, D.; Mohan, M. S. *J. Inorg. Nucl. Chem.* 1965, 27, 1643. Kelm, H.; Harris, G. M. *Inorg. Chem.* 1967, 6, 1743. <sup>c</sup> Calculated from the data of: Kallen, T. W.; Hamm, R. E. *Inorg. Chem.* 1979, 18, 2151. <sup>d</sup>  $\mu = 1.00 \text{ M}$  ( $\text{NaClO}_4$ ). <sup>e</sup>  $\mu = 1.00 \text{ M}$  ( $\text{KNO}_3$ ). <sup>f</sup>  $\mu = 1.00 \text{ M}$  ( $\text{NaNO}_3$ ).

to the form of  $k_{\text{obsd}}$  derived by Kallen and Hamm<sup>3</sup> for data in potassium nitrate media. It also reduces to the form of  $k_{\text{obsd}}$  derived by Kallen<sup>2</sup> for sodium perchlorate media when  $[\text{H}^+] \gg k_{11} k_{31} K_{2b} / k_{21} (k_{10} + k_{10}')$ , eq 16. Therefore, the rate

$$(k_{\text{obsd}})_{\text{NaClO}_4} = (k_1 k_{11} k_{31} / k_2 k_{21}) [\text{HC}_2\text{O}_4^-] + k_{41} [\text{H}^+] \quad (16)$$

constants reported by Kallen<sup>2</sup> for oxalate anation in sodium perchlorate media must be equivalent to  $k_1 k_{11} k_{31} / k_2 k_{21}$ .

Equation 15 cannot be used to evaluate the published data in an exact fashion. However, the aquation rate constant ratio,  $k_{41}'/k_{41}$ , may be estimated by varying  $k_{41}'/k_{41}$  until least-squares analysis of  $[\text{H}^+] (k_{\text{obsd}})_{\text{NaClO}_4} / (k_{\text{obsd}})_{\text{KNO}_3}$  vs.  $[\text{H}^+] / (1 + (k_{41}'/k_{41}) [\text{NO}_3^-])$  gives a linear fit with unit slope as eq 17,

$$\frac{[\text{H}^+] (k_{\text{obsd}})_{\text{NaClO}_4}}{(k_{\text{obsd}})_{\text{KNO}_3}} = \frac{[\text{H}^+]}{1 + (k_{41}'/k_{41}) [\text{NO}_3^-]} + \frac{k_{11} k_{31} K_{2b}}{k_{21} (k_{10} + k_{10}')} \quad (17)$$

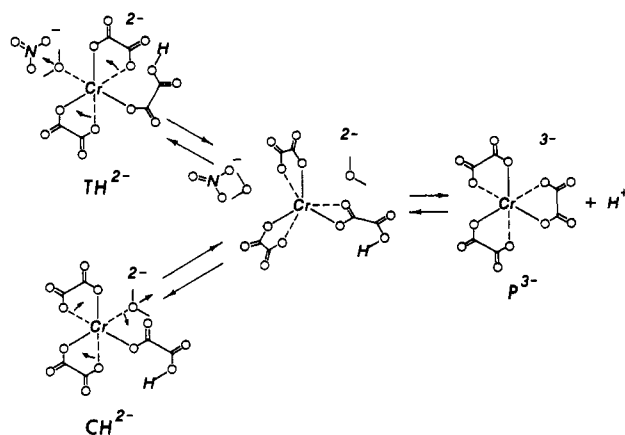
a combined form of eq 15 and 16, suggests. The results of this fitting process and other kinetics parameters derived from the data near pH 1 are summarized in Table VI. Kinetic activation parameters derived specifically from these data have been added to Table V.

The results of our evaluation of the data near pH 1 both support and lend additional insight into the substitution mechanism of *cis*- $\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$ . First, the apparent activation parameters of  $k_1 k_{11} k_{31} / k_2 k_{21}$ ,  $\Delta H^\ddagger = 21.2 \pm 0.2 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -5.4 \pm 0.5 \text{ cal mol}^{-1} \text{ K}^{-1}$  at  $\mu = 1.00 \text{ M}$ , offer strong contrast to those developed for  $k_1 k_{11}' k_{31}' / k_2 k_{21}'$  from data in the pH 3–5 interval ( $\Delta H^\ddagger = 26.1 \pm 0.6 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = 10.6 \pm 1.8 \text{ cal mol}^{-1} \text{ K}^{-1}$  at  $\mu = 1.20 \text{ M}$ ). Clearly the nitrate-catalyzed anation pathway proceeding through *trans*- $\text{Cr}(\text{ox})_2(\text{oxH})(\text{H}_2\text{O})^{2-}$  is a high-enthalpy, high-entropy pathway which can only be important at relatively high temperatures. Activation parameters for the uncatalyzed and nitrate-catalyzed aquation pathways exhibit the same, strong contrast as cyclic thermodynamic considerations require. This parallelism constitutes a particularly satisfying confirmation of our separation of kinetic parameters for the uncatalyzed and nitrate-catalyzed anation processes.

Second, the equilibrium constant for formation of  $\text{Cr}(\text{ox})_3^{3-}$  ( $[\text{Cr}(\text{ox})_3^{3-}] [\text{H}^+] / [\text{cis-Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-] [\text{HC}_2\text{O}_4^-] = 9.55 \pm 0.69$  at 50.0 °C and  $\mu = 1.00 \text{ M}$ )<sup>2</sup> and the value we have derived for  $k_{41}'$  may be used in conjunction with our values of  $k_1$  and  $k_{11}'/k_2$  to estimate  $k_{11}' k_{31}' / k_2 k_{21}'$  and  $k_{31}' / k_{21}'$  as  $0.64 \pm 0.06 \text{ M}^{-2}$  and  $3.2 \pm 0.6 \text{ M}^{-1}$  at 50.0 °C and  $\mu = 1.00 \text{ M}$ . Both values compare favorably with parameters derived from

(20) Stieger, H.; Harris, G. M.; Kelm, H. *Ber. Bunsenges. Phys. Chem.* 1970, 74, 262.

Scheme III



the data in the pH 3-5 interval alone.

Finally, we have used our values of  $k_1$ ,  $k_{11}/k_2$ , and the value of  $k_1 k_{11} k_{31}/k_2 k_{21}$  derived from the data near pH 1 to estimate  $k_{31}/k_{21}$  as  $1.00 \pm 0.06$  at 50.0 °C and  $\mu = 1.00$  M. The small magnitude of this critical rate constant ratio implies that preferential chelation of  $cis\text{-Cr}(\text{ox})_2(\text{oxH})(\text{H}_2\text{O})^{2-}$  from pH 3 to pH 5 is due in fact to rapid chelation of its conjugate base,  $cis\text{-Cr}(\text{ox})_2(\text{-ox})(\text{H}_2\text{O})^{3-}$ . This inference is in accord with the rate relationship observed for chelation of the monodentate oxalato-*O* ligands of  $\text{Cr}(\text{NH}_3)_5(\text{oxH})^{2+}$  and its conjugate base,  $\text{Cr}(\text{NH}_3)_5(\text{-ox})^+$ .<sup>18</sup>

**Nitrate Catalysis.** The rate constant ratio  $k_{31}/k_{21}$  should be independent of ionic strength and reaction medium. Therefore, combined activation data at  $\mu = 1.20$  M and  $\mu = 1.00$  M may be used to estimate its associated activation parameter differences as  $\Delta(\Delta H^\ddagger) = 1.2 \pm 0.5$  kcal mol<sup>-1</sup> and  $\Delta(\Delta S^\ddagger) = 4.0 \pm 1.3$  cal mol<sup>-1</sup> K<sup>-1</sup>. These values emphasize the dissociative character of nitrate-catalyzed chelation when they are compared to  $\Delta(\Delta H^\ddagger) = 4.6 \pm 0.3$  kcal mol<sup>-1</sup> and  $\Delta(\Delta S^\ddagger) = 16.5 \pm 0.8$  cal mol<sup>-1</sup> K<sup>-1</sup> for  $k_{31}'/k_{21}'$ . If the activation parameters for aquation of  $trans\text{-Cr}(\text{ox})_2(\text{oxH})(\text{H}_2\text{O})^{2-}$  ( $k_{21}'$ ) are similar to those for aquation of the acetato-*O* ligand of  $trans\text{-Cr}(\text{ox})_2(\text{OCOCH}_3)(\text{H}_2\text{O})^{2-}$  ( $\Delta H^\ddagger = 16.3$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger = -18.8$  cal mol<sup>-1</sup> K<sup>-1</sup>),<sup>19</sup> nitrate-catalyzed chelation of  $trans\text{-Cr}(\text{ox})_2(\text{oxH})(\text{H}_2\text{O})^{2-}$  ( $k_{31}'$ ) may have activation parameters as large as  $\Delta H^\ddagger = 21$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger = -2$  cal mol<sup>-1</sup> K<sup>-1</sup> ( $k_{31}' \approx 2 \times 10^{-2}$  M<sup>-1</sup> s<sup>-1</sup> at 50.0 °C).

van Eldik and Harris<sup>21</sup> have suggested that the nitrate ion

may catalyze oxalate anation of  $cis\text{-Co}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$  by assisting aqua ligand dissociation. This suggestion appears quite reasonable within our substitution scheme if catalyzed water dissociation acts in concert with an associative rearrangement of the binoxalato-*O* ligand of  $trans\text{-Cr}(\text{ox})_2(\text{oxH})(\text{H}_2\text{O})^{2-}$ . We suggest the detailed mechanism of Scheme III for the nitrate-catalyzed and uncatalyzed chelation processes of  $\text{Cr}(\text{ox})_2(\text{oxH})(\text{H}_2\text{O})^{2-}$ . Here, nitrate-assisted dissociation of the aqua ligand of  $trans\text{-Cr}(\text{ox})_2(\text{oxH})(\text{H}_2\text{O})^{2-}$  leads to the (binoxalato-*O,O*)bis(oxalato-*O,O'*)chromate(III) intermediate common to the chelation mechanism of  $cis\text{-Cr}(\text{ox})_2(\text{oxH})(\text{H}_2\text{O})^{2-}$  and the aquation mechanism of  $\text{Cr}(\text{ox})_3^{3-}$ .<sup>22-25</sup> Coordination isomerization and deprotonation of the binoxalato-*O,O* ligand then produces  $\text{Cr}(\text{ox})_3^{3-}$  in a rapid following step. It should be noted that the higher negative charge of  $trans\text{-Cr}(\text{ox})_2(\text{-ox})(\text{H}_2\text{O})^{3-}$  should make anion-assisted water dissociation less likely. There may indeed be no nitrate-catalyzed chelation step involving this complex ion.

Nitrate catalysis by the Scheme III mechanism will not generalize to all anation processes. In this case, the nitrate ion acts to assist chelation of a potentially bidentate ligand present in the primary coordination sphere of the metal ion. A strong, secondary assist to water dissociation must come from the coordinated ligand itself to make the mechanism function. The fact that the nitrate ion catalyzes chelation, while the chloride ion and perchlorate ion do not, may be due to its particular basicity. It is sufficiently basic that it may interact strongly with the aqua ligand's protons; but it is not so basic that it will deprotonate the aqua ligand or compete favorably for the vacated coordination site.

Nitrate catalysis within this system has served as an extremely useful probe of the overall mechanism for oxalate anation. While the details of the mechanism have been developed by inference, the mathematical constraints placed upon our data evaluation by an additional anation pathway are so great that our ability to infer details has been dramatically increased. We feel that further examination of this and similar reaction systems will only serve to confirm the mechanistic details we have presented here.

**Registry No.**  $cis\text{-Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2$ , 15489-30-2;  $\text{HC}_2\text{O}_4^-$ , 920-52-5;  $\text{C}_2\text{O}_4^{2-}$ , 338-70-5.

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Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

## Alkyldynetricobalt Nonacarbonyl Complexes as Hydroformylation Catalysts

HOWARD P. WITHERS, JR., and DIETMAR SEYFERTH\*

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Several polymerizable alkyldynetricobalt nonacarbonyl complexes,  $(\text{OC})_9\text{Co}_3\text{CC}(\text{O})\text{OCH}_2\text{CH}_2\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$ ,  $(\text{OC})_9\text{Co}_3\text{CC}_6\text{H}_4\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2\text{-}p$ , and  $(\text{OC})_9\text{Co}_3\text{CC}_6\text{H}_4\text{CH}=\text{CH}_2\text{-}p$ , were prepared in order to evaluate their derived polymers and copolymers as hydroformylation catalysts. Partial decomposition of the cluster occurs under the reaction conditions. The mono- and/or dinuclear cobalt carbonyl species that are formed appear to be the actual hydroformylation catalysts, contrary to earlier interpretation.

### Introduction

Ryan, Pittman, and O'Connor,<sup>1</sup> during the course of investigations of the possibility of "metal cluster catalysis",<sup>2</sup>

reported that benzylidynetricobalt nonacarbonyl (**1**) is an effective hydroformylation catalyst or catalyst precursor. The cluster complex, they said, was "recovered unchanged in high

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