Compounds", Academic Press, New York, N.Y., 1970.
(4) A. Davison and J. E. Ellis, *J. Organomet. Chem.*, **31**, 239 (1971).
(5) N. A. Beach and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 5713 (1968).
(6) M. Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, **5**, 165 (1973).
(7) (a) M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc. A*, 2939 (1971); (b) A. G. Massey and L. E. Orgel, *Nature (London)*, **191**, 1387 (1961); (c) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Am. Chem. Soc.*, **84**, 3589 (1962); **85**, 1013 (1963); (d) J. Nasielski, P. Kirsch, and L. Wilputte-Steinert, *J. Organomet. Chem.*, **29**, 269 (1971); (e) J. M. Kelly, H. Hermann, and E. A. Koerner von Gustorf, *J. Chem. Soc., Chem. Commun.*, 105 (1973); (f) J. A. McIntyre, *J. Phys. Chem.*, **74**, 2403 (1970).
(8) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Interscience, New York, N.Y., 1972, pp 770–800.
(9) (a) M. S. Wrighton, D. S. Ginley, M. A. Schroeder, and D. L. Morse, *Pure Appl. Chem.*, **41**, 671 (1975); (b) M. S. Wrighton and M. A. Schroeder, *J. Am. Chem. Soc.*, **96**, 6235 (1974); **95**, 5764 (1973); (c) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Organomet. Chem.*, **70**, 283 (1974); *J. Am. Chem. Soc.*, **92**, 6068 (1970); **93**, 3285 (1971); (d) W. Jennings and B. Hill, *ibid.*, **92**, 3199 (1970); (e) B. Hill, K. Math, D. Pillsbury, B. Voecks, and W. Jennings, *Mol. Photochem.*, **5**, 195 (1973); (f) J. Nasielski, P. Kirsch, and L. Wilputte-Steinert, *J. Organomet. Chem.*, **27**, C13 (1971); (g) G. Platobrood and L. Wilputte-Steinert, *ibid.*, **70**, 393, 407 (1974); (h) P. Krausz, F. Garnier, and J. E. Dubois, *J. Am. Chem. Soc.*, **97**, 437 (1975); (i) A. Agapiou and E. McNelis, *J. Chem. Soc., Chem. Commun.*, 187 (1975).
(10) (a) E. P. Kündig, D. McIntosh, M. Moskovits, and G. A. Ozin, *J. Am. Chem. Soc.*, **95**, 7234 (1973); (b) E. P. Kündig and G. A. Ozin, *ibid.*, **96**, 3820 (1974); (c) H. Huber, E. P. Kündig, and G. A. Ozin, *ibid.*, **96**, 5585 (1974); (d) H. Huber, E. P. Kündig, G. A. Ozin, and A. J. Poë, *ibid.*, **97**, 308 (1975); (e) G. A. Ozin, H. Huber, E. P. Kündig, and M. Moskovits, *ibid.*, **97**, 2097 (1975).
(11) R. Perutz, Ph.D. Thesis, University of Newcastle-upon-Tyne, 1974.
(12) M. S. Wrighton, D. S. Ginley, and D. L. Morse, *J. Phys. Chem.*, **78**, 2229 (1974).
(13) P. S. Braterman and A. Fullarton, *J. Organomet. Chem.*, **31**, C27 (1971).
(14) K. W. Hipps and G. A. Crosby, *Inorg. Chem.*, **13**, 1543 (1974).
(15) M. Mingardi and G. B. Porter, *J. Chem. Phys.*, **44**, 4354 (1966).
(16) M. S. Wrighton, L. Pdungsap, and D. L. Morse, *J. Phys. Chem.*, **79**, 66 (1975).
(17) M. S. Wrighton, D. L. Morse, H. B. Gray, and D. K. Ottesen, *J. Am. Chem. Soc.*, in press.
(18) M. K. De Armond, *Acc. Chem. Res.*, **7**, 309 (1974), and references therein.
(19) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **93**, 4336 (1971).
(20) (a) G. Malouf and P. C. Ford, *J. Am. Chem. Soc.*, **96**, 601 (1974); (b) D. S. Chaisson, R. E. Hintze, D. H. Stuermer, J. D. Petersen, D. P. McDonald, and P. C. Ford, *ibid.*, **94**, 6665 (1972).
(21) J. E. Ellis, Ph.D. Thesis, M.I.T., 1966.
(22) F. G. Moses, R. S. H. Liu, and M. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).
(23) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

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Reactions of the *trans*- and *cis*-Diaquobis(oxalato)chromate(III) Ions in Solutions Which Contain Oxalic Acid

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When *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ is added to acidic solutions that contain $H_2C_2O_2$ and $HC_2O_4^-$, rapid isomerization of the trans complex occurs. This step is followed by the slower anation of the resulting cis complex by oxalate species. Anation proceeds to an equilibrium mixture of species described by the equilibrium quotient $K_3 = [Cr(C_2O_4)_3{}^{3-}][H^+]^2/[cis\text{-}Cr(C_2O_4)_2(H_2O)_2{}^-][H_2C_2O_4]$. At 50°C and $\mu = 1.00\ M$, maintained with potassium nitrate, $K_3 = 0.890 \pm 0.012\ M$. The kinetics of the two-step reaction at $\mu = 1.00\ M$, between 35 and 55°C, are reported. Both steps of the reaction obey simple first-order kinetics. Observed pseudo-first-order rate constants for the trans–cis isomerization in sodium perchlorate and potassium nitrate were fit to the form $k_{obsd} = k_{H_2O} + k_M[M^+] + k_H[H^+]$, where M is sodium or potassium. Activation enthalpies for the various constants are 15.1 ± 0.5 (k_{Na}), 14.7 ± 0.8 (k_K), and 18.5 ± 0.3 (k_H) kcal/mol. Activation entropies are -23.9 ± 1.6 (k_{Na}), -26.0 ± 2.6 (k_K), and -8.5 ± 0.8 (k_H) cal/(mol deg). Data interpretations are based on $\Delta H^\ddagger = 17.9$ kcal/mol and $\Delta S^\ddagger = -14.7$ cal/(mole deg) for k_{H_2O}. Hydrogen ion and ligand dependencies of the observed pseudo-first-order anation rate constants are medium-dependent and slower rates are observed in perchlorate media. In perchlorate media, $k_{obsd} = k_b[HC_2O_4^-] + k_4[H^+]$, while in nitrate media, $k_{obsd} = \{k_1[H_2C_2O_4] + (k_2k_4/k_3)[H^+]^2\}/\{1 + (k_2/k_3)[H^+]\}$. At 50°C in potassium nitrate, $k_1 = 2.84 \times 10^{-2}\ M^{-1}\ sec^{-1}$, $k_2/k_3 = 73.8 \pm 11.3\ M^{-1}$, and $k_4 = 4.38 \times 10^{-4}\ M^{-1}\ sec^{-1}$. Activation enthalpies are 20.7 ± 0.4 and 21.9 ± 0.4 kcal/mol, and activation entropies are -1.9 ± 1.0 and -6.5 ± 1.4 cal/(mol deg), for k_1 and k_4, respectively. A steady-state mechanism, which describes k_1 and k_3 as anation steps and k_2 and k_4 as aquation steps, is proposed for the anation reaction in both media. This mechanism identifies k_b as a composite constant equal to k_1k_3/k_2K_1, where K_1 is the first dissociation constant of oxalic acid. The anation rate constant, k_1, is limited by k_H for the trans–cis isomerization. Other mechanistic similarities between the isomerization process and aquation and anation processes are described, and a new conformation for the bidentate oxalate ligand is proposed as a precursor to each process.

Introduction

The trans–cis isomerization of $Cr(C_2O_4)_2(H_2O)_2^-$ has been investigated by a variety of research groups. Uncatalyzed pathways,[1,2] hydrogen ion catalyzed pathways,[3-5] multivalent cation catalyzed pathways,[5] and univalent cation catalyzed pathways[6] have been identified for this superficially simple process. Isomerization is generally thought to involve generation of a half-bonded oxalate intermediate which may be stabilized by association with a hydrogen ion or other cations. Operation of the deuterium isotope effect upon the hydrogen ion catalyzed pathway, for example, may be explained by a preequilibrium involving the hydrogen ion, followed by a rate-determining step which is not subject to an isotope effect.

The anation reaction of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ with oxalate species is not as well characterized. Anation reactions involving the oxalate ion[7,8] and hydrogen oxalate ion[8] have been examined and an ion-pairing mechanism was proposed to rationalize the dependence of the rate upon the ligand concentration.[8]

Aquation of $Cr(C_2O_4)_3{}^{3-}$ to the *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ complex ion has been studied under a wide variety of conditions, with the majority of investigators agreeing upon a two-term rate law which involves first- and second-order hydrogen ion catalysis.[9-12] The deuterium isotope effect,

Table I. Values of the First Acid Dissociation Constant for Oxalic Acid, Determined in $NaClO_4$ and KNO_3 at $\mu = 1.00\ M^a$

T, °C	pK_1 ($NaClO_4$)	pK_1 (KNO_3)
35.0		1.036 ± 0.015
40.0	1.027 ± 0.008	0.961 ± 0.020
45.0	1.044 ± 0.018	1.045 ± 0.006
50.0	1.025 ± 0.008	1.001 ± 0.011
55.0	1.063 ± 0.043	1.047 ± 0.028

[a] Average of all determinations: p$K_1 = 1.03 \pm 0.03$, or $K_1 = 0.0933\ M$.

operating upon the aquation rate, causes rate changes which again may be interpreted in terms of hydrogen ion involvement in an equilibrium preceding the rate-determining step.[9] Activation energies for aquation and anation seem to be almost identical[11] and are 3–4 kcal/mol greater than the activation energies for uncatalyzed and hydrogen ion catalyzed isomerization.[5,6]

Recent investigations have determined a rate for water exchange of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ which is slower than the rate of anation or trans–cis isomerization.[13,14] Unusually large ion-pairing equilibrium constants would be required to justify a water-exchange mechanism for anation. Therefore, there is a need for the reexamination of the anation mechanism for *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$. Alternate mechanisms for entry of oxalate species into the coordination sphere of chromium(III) must be evaluated. If one considers the similarity of the activation parameters for anation and aquation, it would be desirable to derive a mechanistic link between the two processes; and, if similarities in the postulated reaction intermediates are considered, it would also be desirable to link the isomerization and aquation mechanisms. With these considerations in mind, we must also suspect a mechanistic link between isomerization and anation.

We consider the most reasonable site for attack of an entering ligand to be the coordinated oxalate ligands, themselves, and the most reasonable activated complex to be a variant of the isomerization or aquation intermediate. We have therefore examined the trans–cis isomerization and the reaction of oxalate species with *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ in a pH region where the more acidic species, oxalic acid, is present to activate isomerization and anation pathways. The results of this study clarify the mechanistic relationship between isomerization, aquation, and anation.

Experimental Section

The *trans*-$KCr(C_2O_4)_2(H_2O)_2{\cdot}3H_2O$ and $K_3Cr(C_2O_4)_3{\cdot}3H_2O$ complex salts were prepared by Werner's methods[15] and were analyzed for chromium and oxalate. Anal. Calcd for $KCr(C_2O_4)_2(H_2O)_2{\cdot}3H_2O$: Cr, 14.56; $C_2O_4^{2-}$, 49.3. Found: Cr, 14.67 ± 0.02; $C_2O_4^{2-}$, 49.4 ± 0.2. Calcd for $K_3Cr(C_2O_4)_3{\cdot}3H_2O$: Cr, 10.67; $C_2O_4^{2-}$, 54.2. Found: Cr, 10.76 ± 0.02; $C_2O_4^{2-}$, 54.4 ± 0.2. Chromatographed samples of the *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ complex ion in nitric acid–potassium nitrate media and their analyses were obtained by methods described earlier.[16]

Solutions for the rate determinations and equilibrium studies were prepared from solid sodium or potassium oxalate, oxalic acid dihydrate, and standard 2 M solutions of sodium perchlorate, perchloric acid, potassium nitrate, and nitric acid.

The hydrogen ion concentration of each prepared solution was determined with a pH meter which had been standardized to give a linear response to pcH between pcH = 0.700 and pcH = 2.000 at an ionic strength of 1.00 M. Values of the hydrogen ion concentation, the analytical oxalate concentration, C_{ox}, and the formal concentrations of oxalic acid dihydrate and sodium or potassium oxalate were then used to calculate the equilibrium quotient for the first dissociation of oxalic acid, $K_1 = [H^+][HC_2O_4^-]/[H_2C_2O_4]$. Values of p$K_1$ derived by this method are listed in Table I. Since pK_1 was virtually invariant, despite medium and temperature changes, an average value of pK_1 = 1.03 ± 0.03 (K_1 = 0.0933 M) was used to compute equilibrium concentrations of all species between 35 and 55°C in sodium perchlorate and potassium nitrate. Moorhead and Sutin[17] have determined a value of $K_1 = 0.084 \pm 0.002$ at 25°C and an ionic strength of 1.0 M. Considering the temperature variation data of Bauer and Smith[18] at an ionic strength of 0.50 M, our value is appropriate for the indicated temperature range.

Table II. Equilibrium Measurements on the System

$$cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- + H_2C_2O_4 \overset{K_3}{\rightleftharpoons} Cr(C_2O_4)_3^{3-} + 2H_3O^+$$

at 50° C and $\mu = 1.00\ M$ in Potassium Nitrate

10^3T_0, F^a	A_{570}, au cm^{-1}	$[H^+]$, M	$[H_2C_2O_4]$, M^b	K_3, M^c
4.88	0.261	0.792	0.0933	0.881
4.90	0.267	0.692	0.0923	0.879
4.91	0.274	0.593	0.0900	0.899
4.88	0.281	0.493	0.0874	0.909
4.89	0.292	0.394	0.0836	0.899
4.90	0.308	0.295	0.0781	0.883
4.89	0.330	0.197	0.0692	0.873
4.89	0.359	0.099	0.0520	0.895

[a] Added as $K_3Cr(C_2O_4)_3{\cdot}3H_2O$. [b] Initial formality = 0.100 F. [c] Calculated as $K_3 = (A_{570} - 50.2T_0)[H^+]^2/(78.4T_0 - A_{570})(H_2C_2O_4]$, where 50.2 and 78.4 M^{-1} cm^{-1} are the molar absorptivities of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ and $Cr(C_2O_4)_3^{3-}$ at 570 nm.

The oxalate content of the complex salts and the purity of the oxalic acid dihydrate were determined by the method of Hamm.[2] Sodium oxalate and potassium oxalate were used, without analysis, after being dried at 100°C. Perchloric and nitric acid concentrations were determined by titration with standard 0.1 N sodium hydroxide. Stock salt solutions were standardized by exchanging the cation of an aliquot for H^+ on a column of Dowex 50W-X8 (50–100 mesh) cation-exchange resin. The resulting acid solution was titrated with standard 0.1 N sodium hydroxide to determine the number of milliequivalents of K^+ or Na^+ exchanged per milliliter of stock solution introduced to the resin. Chromium was determined after oxidation to chromium(VI) with potassium peroxydisulfate in 1 M sulfuric acid. Chromium(VI) was reduced to chromium(III) with an excess of standard 0.1 N ferrous ammonium sulfate and the excess ferrous ion was back-titrated with standard 0.1 N potassium dichromate to a diphenylaminesulfonate end point.

Spectrophotometric rate determinations were made at 570 nm, using a Guilford Model 240 spectrophotometer which was serviced by a Lauda K2/R circulating water bath. Temperature in the cell block was checked at the start and end of each set of three kinetic runs and was found to be constant within ±0.1°. Reactions were initiated by adding finely ground *trans*-$KCr(C_2O_4)_2(H_2O)_2{\cdot}3H_2O$ to 25.0 ml of temperature-equilibrated reagent solution. After stirring of this solution for 45 sec, a portion was transferred by syringe to a temperature-equilibrated cuvette in the cell block. Initial concentrations of the trans complex were $2.5 \times 10^{-3}\ M$ at the lowest total oxalate concentration, C_{ox}, and $5.0 \times 10^{-3}\ M$ at all other values of C_{ox}. "Infinite time" absorbance measurements were made at the time estimated as 10 half-lives for the slow reaction and were checked 8–12 hr later.

Rate constants were evaluated graphically from semilogarithmic plots of $(A_\infty - A)$ vs. t. These plots had an early curved portion, followed by a portion which was linear to at least 3 half-lives on the slower rate. Such behavior is indicative of, but not absolute proof of, the existence of two, consecutive steps to the reaction process. We have used the method outlined by Ashley and Hamm[19] to derive rate constants for the fast step, k_f, and the slow step, k_s, of the reaction sequence. Duplicate rate determinations were made at each set of conditions and average values of the rate constants are reported. The average deviation in k_s averaged ±2%, while the average deviation of k_f was at most ±4% and averaged ±3%.

The reaction of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ in acidic media containing oxalate species proceeds to an equilibrium mixture of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ and $Cr(C_2O_4)_3^{3-}$. Values of the equilibrium quotient, $K_3 = [Cr(C_2O_4)_3^{3-}][H^+]^2/[Cr(C_2O_4)_2(H_2O)_2^-][H_2C_2O_4]$, have been determined at 50°C over a wide variety of hydrogen ion concentrations, an oxalic acid formality of 0.1 F, and an ionic strength of 1.00 M, maintained with potassium nitrate. $K_3Cr(C_2O_4)_3{\cdot}3H_2O$ was added to the solutions to provide a total chromium concentration, T_0, of ca. $5 \times 10^{-3}\ M$. The solutions were then equilibrated for 18 hr at 50.0°C. The ratio of concentrations, given by $f = [Cr(C_2O_4)_3^{3-}]/[cis\text{-}Cr\text{-}$

$(C_2O_4)_2(H_2O)_2^-]$, was determined from absorbance measurements at 570 nm, as $f = (A_{570} - 50.2T_0)/(78.4T_0 - A_{570})$. Here, 50.2 and 78.4 M^{-1} cm^{-1} are the molar absorptivities at 570 nm of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ and $Cr(C_2O_4)_3^{3-}$ and A_{570} is the measured absorbance. Equilibrium oxalic acid and hydrogen ion concentrations were determined from the quantity of oxalate released and initial formalities. Results of these determinations, given in Table II, lead to an average value of $K_3 = 0.890 \pm 0.012$ *M*. The quotient K_3/K_1, which corresponds to that for equilibration with $HC_2O_4^-$, would therefore have a value of 9.55 ± 0.85, rather than 14 as estimated by Kelm and Harris[11] from anation data in potassium nitrate and aquation data in sodium perchlorate.

Results

If the general sequence of the reaction of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ in acidic, oxalic acid containing media is assumed to be described by eq 1, the equation derived for the

$$\textit{trans}\text{-}Cr(C_2O_4)_2(H_2O)_2^- \xrightarrow{k_f} \textit{cis}\text{-}Cr(C_2O_4)_2(H_2O)_2^- \underset{k_s''}{\overset{k_s'}{\rightleftharpoons}} Cr(C_2O_4)_3^{3-} \quad (1)$$

change in absorbance with time would be given by eq 2. Here,

$$A_\infty - A = \chi_1 \exp(-k_f t) + \frac{(A_\infty - \epsilon_{cis}T_0)k_f}{k_f - k_s} \exp(-k_s t) \quad (2)$$

T_0 is the initial concentration of the trans complex, the constant k_s is equal to the sum of k_s' and k_s'', χ_1 is a complex function of molar absorptivities and rate constants, and ϵ_{cis} is the molar absorptivity of the cis complex. At large values of the time, *t*, a plot of ln $(A_\infty - A)$ vs. *t* would become linear, with slope of $-k_s$ and a "time zero" intercept of ln $[(A_\infty - \epsilon_{cis}T_0)k_f/(k_f - k_s)]$. We have used the derived values of k_f and k_s and the "time zero" intercept to calculate ϵ_{cis} for each of the rate determinations. At 570 nm in sodium perchlorate media, $\epsilon_{cis} = 50.2 \pm 0.7$ M^{-1} cm^{-1}. In potassium nitrate media, $\epsilon_{cis} = 49.9 \pm 0.6$ M^{-1} cm^{-1}. Since *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ has a molar absorptivity of 50.2 ± 0.4 M^{-1} cm^{-1} at this wavelength, eq 1 is in all probability an accurate representation of the overall, observed reaction.

Rate determinations were made at an ionic strength of 1.00 *M*, maintained with sodium perchlorate or potassium nitrate. Oxalic acid was the sole oxalate-containing species added at 35, 40, 45, and 55°C, such that $[H^+] = [HC_2O_4^-]$ for all points at these temperatures. Sodium or potassium oxalate was added with oxalic acid for several rate determinations at 50°C to provide a series of points at an approximately constant hydrogen ion concentration of 0.06 *M*. Data, including he rate constants for the fast and slow steps of the reaction, are summarized in Table III.

Data for the fast step in the overall process at 50°C, in both sodium perchlorate and potassium nitrate media, show the rate of this process to be dependent upon the hydrogen ion concentration and independent of the concentrations of oxalate species. Rate constants for the process, k_f of Table III, were fit to the equation $k_f = k_a[H^+] + k_a'$ by a linear least-squares evaluation. The resulting values of k_a and k_a' are given in Table IV.

Values of k_f were sufficiently similar to those projected from the data of Kelm, Stieger, and Harris[5,6] for the isomerization of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ that we have also determined comparative rate constants for the isomerization, alone. Values of k_a and k_a' derived from rate constants obtained at 25 and 35°C are summarized in Table IV. Hydrogen ion concentrations for these rate determinations ranged from 0.01 to 0.50 *M* at 25°C and from 0.01 to 0.25 *M* at 35°C. Direct correlation of k_a and k_a' for the isomerization reaction and for the fast step of the overall process at 35°C in potassium nitrate completes the identification of the fast step as the trans–cis isomerization of $Cr(C_2O_4)_2(H_2O)_2^-$. A similar, excellent correlation between processes is obtained by extrapolation of k_a and k_a' for the reaction in the presence of oxalate species to 25 and 35°C, using an Arrhenius activation energy plot.

Data for the slow step of the process in sodium perchlorate are also easily analyzed. The rate constant, k_s, is directly proportional to the hydrogen oxalate concentration at 40, 45,

Table III. Pseudo-First-Order Rate Constants for the Slow and Fast Steps in the Reaction of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ in Acidic, Oxalic Acid Containing Media

			$NaClO_4$[a]		KNO_3[a]	
T, °C	C_{ox}, *F*[b]	$[H^+]$, *M*[c]	10^3k_f, sec^{-1}	10^5k_s, sec^{-1}	10^3k_f, sec^{-1}	10^5k_s, sec^{-1}
35.0	0.05	0.0361			1.49	2.26
	0.10	0.0606			1.66	4.21
	0.15	0.0805			1.76	5.86
	0.20	0.0977			1.89	7.29
40.0	0.05	0.0361	2.77	2.78	2.38	3.98
	0.10	0.0606	3.06	4.62	2.57	7.31
	0.1375	0.0758			2.90	9.64
	0.15	0.0805	3.24	6.16		
	0.20	0.0977	3.48	7.64	3.05	12.7
	0.25	0.1130			3.22	15.1
45.0	0.05	0.0361	4.24	4.90	3.65	6.67
	0.10	0.0606	4.70	8.24	4.04	12.1
	0.15	0.0805	5.01	10.8	4.38	17.0
	0.20	0.0977	5.30	13.4	4.68	21.6
	0.25	0.1130	5.53	15.3		
	0.30	0.1270			5.11	28.4
50.0	0.05	0.0361	6.19	8.12	5.86	11.9
	0.10	0.0606	6.87	13.5	6.50	22.5 (22.6)
	0.13[d]	0.0627[e]	7.08	17.8	6.48	28.7 (28.7)
	0.15[d]	0.0640[f]	6.90	19.9	6.69	32.5 (32.6)
	0.18[d]	0.0657[g]	6.98	23.2	6.78	38.3 (38.5)
	0.20[d]	0.0667[h]	7.20	26.1	6.84	40.9 (42.4)
	0.20	0.0977	7.89	22.1	7.50	39.4
	0.20[i]	0.0977	8.08[j]	26.8[j]	7.95[k]	39.4[k]
	0.20[i]	0.0977	7.96[l]	31.6[l]	7.88[m]	36.0[m]
	0.30	0.1270	8.90	29.6	8.30	53.1
	0.40	0.1521	9.20	35.4	9.06	63.0
55.0	0.05	0.0361	9.67	13.9	8.54	20.4
	0.10	0.0606	11.0	23.3	9.64	38.4
	0.20	0.0977	12.2	37.8	11.4	66.6
	0.30	0.1270	14.0	49.0	12.8	89.4
	0.40	0.1521	14.3	58.8	14.2	109.

[a] Supporting electrolyte, $\mu = 1.00$ *M*. [b] The total concentration of oxalate species, added as oxalic acid. [c] Calculated, using $K_1 = 0.0933$ *M*; $[H^+] = [HC_2O_4^-]$. [d] Oxalic acid and $K_2C_2O_4$ or $Na_2C_2O_4$ added. [e] Hydrogen oxalate concentration 0.0777 *M*. [f] Hydrogen oxalate concentration 0.0890 *M*. [g] Hydrogen oxalate concentration 0.1057 *M*. [h] Hydrogen oxalate concentration 0.1167 *M*. [i] In mixed electrolytes. [j] $[NaClO_4] = 0.645$ *M*; $[NaNO_3] = 0.250$ *M*. [k] $[NaNO_3] = 0.895$ *M*. [l] $[NaClO_4] = 0.395$ *M*; $[NaNO_3] = 0.500$ *M*. [m] $[NaClO_4] = 0.145$ *M*; $[NaNO_3] = 0.750$ *M*.

Table IV. Derived Rate Constants for the Isomerization of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ in Acidic, Oxalic Acid Containing Media[a]

T, °C	Medium[a]	10^3k_a, M^{-1} sec^{-1}	$10^3k_a'$, sec^{-1}
25.0	$NaClO_4$[b,d]	2.25 ± 0.08[c]	0.569 ± 0.024[c]
35.0	$NaClO_4$[b,e]	6.46 ± 0.13	1.52 ± 0.02
40.0	$NaClO_4$	11.3 ± 0.6	2.36 ± 0.04
45.0	$NaClO_4$	16.7 ± 0.4	3.66 ± 0.03
50.0	$NaClO_4$	26.8 ± 1.3	5.28 ± 0.11
55.0	$NaClO_4$	44.1 ± 3.6	8.34 ± 0.38
25.0	KNO_3[b,d]	2.23 ± 0.04	0.476 ± 0.013
35.0	KNO_3[b,e]	6.48 ± 0.19	1.25 ± 0.03
35.0	KNO_3	6.35 ± 0.31	1.26 ± 0.02
40.0	KNO_3	11.2 ± 1.1	1.96 ± 0.09
45.0	KNO_3	16.2 ± 0.3	3.07 ± 0.03
50.0	KNO_3	27.1 ± 0.8	4.91 ± 0.07
55.0	KNO_3	48.5 ± 1.0	6.73 ± 0.10

[a] $\mu = 1.00$ *M*; $k_f = k_a[H^+] + k_a'$. [b] Results in the absence of added $H_2C_2O_4$ or $HC_2O_4^-$. [c] Standard deviation of the rate constant. [d] $[H^+]$ varied from 0.01 to 0.50 *M*. [e] $[H^+]$ varied from 0.1 to 0.25 *M*.

Table V. Derived Rate Constants for the Reaction of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ in Sodium Perchlorate Media Containing $H_2C_2O_4$ and $HC_2O_4^-$ [a]

T, °C	10^4k_4, M^{-1} sec^{-1} [b]	10^4k_b, M^{-1} sec^{-1} [c]	K[d]
40.0	0.73	6.97 ± 0.09	9.55
45.0	1.3	12.3 ± 0.1	9.46
50.0	2.2	20.7 ± 0.4	9.41
55.0	3.7	34.9 ± 0.1	9.43
E_{act}[e]	22.2	21.9 ± 0.2	

[a] Observed rate constant, $k_s = k_b[HC_2O_4^-] + k_4[H^+]$. [b] Calculated, using $\Delta H^{\ddagger} = 21.6$ kcal/mol[10] and $k_4 = 2.2 \times 10^{-4}\ M^{-1}$ sec^{-1} at 50°C.[11] [c] Calculated as $(k_s - k_4[H^+])/[HC_2O_4^-]$. [d] $K = [Cr(C_2O_4)_3^{3-}][H^+]/[cis\text{-}Cr(C_2O_4)_2(H_2O)_2^-][HC_2O_4^-] = k_b/k_4$. [e] Units are kcal/mol.

Table VI. Derived Rate Constants for the Reaction of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ in Potassium Nitrate Media Which Contain $H_2C_2O_4$ and $HC_2O_4^-$ [a]

T, °C	10^3k_1, M^{-1} sec^{-1}	k_2/k_3, M^{-1}	10^5k_4, M^{-1} sec^{-1}
35.0	5.66	79.6 ± 2.4	8.02
40.0	9.65	77.1 ± 7.9	14.1
45.0	16.0	76.6 ± 11.3	23.6
50.0	28.4	73.8 ± 11.3	43.8
55.0	46.8	71.0 ± 1.6	75.0
$\Delta H^{\ddagger}$ [b]	20.7 ± 0.3		21.9 ± 0.4
$\Delta S^{\ddagger}$ [c]	−1.9 ± 1.0		−6.5 ± 1.4

[a] Observed rate constant $k_s = \{k_1[H_2C_2O_4] + (k_2k_4/k_3)\cdot[H^+]^2\}/\{1 + (k_2/k_3)[H^+]\}$. [b] Units are kcal/mol. [c] Units are cal/(mol deg).

50, and 55°C and shows no additional hydrogen ion dependence. Comparison of 50°C data at constant and variable hydrogen ion concentrations would seem to preclude the presence of a substantial hydrogen ion dependent aquation term. However, we have fit k_s to the equation $k_s = k_b\cdot[HC_2O_4^-] + k_4[H^+]$. Values of k_4 were estimated by using k' of Kelm and Harris' aquation study[11] and the activation enthalpy derived by Banerjea and Mohan for k'.[10] Estimated values of k_4 and derived values of k_b are given in Table V.

We have also calculated values of the equilibrium quotient for anation by the hydrogen oxalate ion, $K = [Cr(C_2O_4)_3^{3-}][H^+]/[cis\text{-}Cr(C_2O_4)_2(H_2O)_2^-][HC_2O_4^-]$, at each temperature as $K = k_b/k_4$. These values are remarkably close to our determined quotient, $K_3/K_1 = 9.55 \pm 0.85$, at 50°C, and lend support to the validity of our method of partitioning k_s in sodium perchlorate media.

Data for the slow-step rate constant, k_s, in potassium nitrate media do not obey the simple relationship observed in sodium perchlorate media. Rather, these data may be fit to $k_s = kKC_{ox}/(1 + KC_{ox})$ with a fair degree of success. However, this expression cannot be justified by an appropriate equilibration mechanism which would generalize to the sodium perchlorate case *and* include aquation pathways for the $Cr(C_2O_4)_3^{3-}$ complex ion. We have therefore fit the potassium nitrate data to eq 3. The fitting process was accomplished

$$k_s = \frac{k_1[H_2C_2O_4] + (k_2k_4/k_3)[H^+]^2}{1 + (k_2/k_3)[H^+]} \qquad (3)$$

by a least-squares evaluation of $[H^+]^2/k_s$ vs. $[H^+]$ for data where $[H^+] = [HC_2O_4^-]$. Such an evaluation yields $(k_1/K_1 + k_2k_4/k_3)^{-1}$ as the intercept and (k_2/k_3) as the ratio of the slope to the intercept. Since the reciprocal of the intercept may be written as $(k_2k_4/k_3)(K_3/K_1 + 1)$, we were able to partition the intercept term into its corresponding anation term, k_1, and aquation term, k_4, by appropriate use of the equilibrium constants of Table V. Values derived for k_1, k_2/k_3, and k_4 by this method and the activation parameters of k_1 and k_4 are given in Table VI. Values calculated for k_s at constant hydrogen ion concentration using eq 3 and the data of Table VI are included in parentheses in Table III. The excellent correlation obtained at constant hydrogen ion concentration attests to the validity of the partitioning process.

The apparent acceleration of k_s in nitrate media and the different forms of the anation rate law in sodium perchlorate and potassium nitrate led us to include rate determinations in which the nitrate concentration was varied substantially. Rate determinations were made at 50°C, a constant analytical oxalate concentration of 0.20 F, and a hydrogen ion concentration of 0.0933 M. The sum of the sodium perchlorate and sodium nitrate concentrations was maintained at 0.895 M to provide a constant ionic strength of 1.00 M. The rate constant, k_s, had the same value in 0.895 M sodium nitrate that was observed in 0.895 M potassium nitrate; and k_f was unaffected by the substitution of nitrate for perchlorate. The anation rate constant, k_s, increased in a linear fashion with increases in the nitrate concentration. The variation in k_s may be described quite accurately by the equation $k_s = [(19.1 \pm 0.4) \times 10^{-5}\ M^{-1}\ \text{sec}^{-1}][NO_3^-] + [(22.0 \pm 0.2) \times 10^{-5}\ \text{sec}^{-1}]$. Data for these rate determinations are included as footnoted entries in Table III.

Discussion

Kelm, Stieger, and Harris[5,6] have shown the trans–cis isomerization of $Cr(C_2O_4)_2(H_2O)_2^-$ to be subject to general metal ion catalysis, as well as hydrogen ion catalysis, and have determined a form for the observed rate constant for isomerization which is given by eq 4. The mechanism for the

$$k_f = k_{H_2O} + k_M[M^+] + k_H[H^+] \qquad (4)$$

isomerization reaction was given in detailed form by eq 5–7.

$$trans\text{-}Cr(C_2O_4)_2(H_2O)_2^- \xrightarrow{k_{H_2O}} cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- \qquad (5)$$

$$trans\text{-}Cr(C_2O_4)_2(H_2O)_2^- + M^+ \xrightarrow{k_M} cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- + M^+ \qquad (6)$$

$$trans\text{-}Cr(C_2O_4)_2(H_2O)_2^- + H^+ \xrightarrow{k_H} cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- + H^+ \qquad (7)$$

Each of the processes has been written as an unidirectional reaction because estimates of the isomerization equilibrium constant strongly favor the cis form.[20]

When ionic strength is maintained at 1.00 M by simultaneously varying the hydrogen ion concentration and supporting, univalent cation concentration, eq 4 reduces to our observed form, $k_f = k_a[H^+] + k_a'$, where $k_a = k_H - k_M$ and $k_a' = k_{H_2O} + k_M$. We have used Kelm's data[5,6] to derive values of k_{H_2O} at an ionic strength of 1.00 M and the temperatures of our study. These values and the data of Table IV were then used to calculate values of k_M for Na^+ and K^+ and values of k_H in sodium perchlorate and potassium nitrate media. The results of these computations and activation parameters for each of the constants are given in Table VII. The isomerization parameters of Table VII should be more representative of the individual processes than those previously reported,[6] since the constants were previously calculated using rate constants which contained a small to moderate k_{H_2O} term.

The hydrogen ion catalyzed pathway has the same activation parameters in the two media, within experimental error. This result rules out specific anion effects or serious activity effects on the isomerization process. When data from both media are combined, $\Delta H^{\ddagger} = 18.5 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -8.5 \pm 0.8$ cal/(mol deg).

In spite of causing a decrease in the isomerization activation enthalpy, sodium and potassium ion catalyses are relatively ineffective due to a large accompanying decrease in the activation entropy. Hydrogen ion catalysis, on the other hand, is exceptionally effective due to an increase in the activation

Table VII. Detailed Kinetic Parameters for the Isomerization of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ in Acidic, Oxalic Acid Containing Media[a]

		NaClO$_4$		KNO$_3$	
T, °C	$10^3k_{H_2O}$, sec^{-1} [c]	10^3k_{Na}, M^{-1} sec^{-1} [d]	10^3k_H, M^{-1} sec^{-1} [e]	10^3k_K, M^{-1} sec^{-1} [d]	10^3k_H, M^{-1} sec^{-1} [e]
25.0[b]	0.278	0.291	2.54	0.198	2.43
35.0[b]	0.767	0.753	7.21	0.483	6.96
35.0	0.767			0.493	6.84
40.0	1.24	1.12	12.4	0.720	11.9
45.0	1.98	1.68	18.4	1.09	17.3
50.0	3.12	2.16	29.0	1.79	28.9
55.0	4.84	3.50	47.6	1.89	50.4
$\Delta H^\ddagger$ [f]	17.9 ± 0.5[h]	15.1 ± 0.5	18.2 ± 0.3[i]	14.7 ± 0.8	18.7 ± 0.4[i]
$\Delta S^\ddagger$ [g]	−14.7	−23.9 ± 1.6	−9.3 ± 0.9[i]	−26.0 ± 2.6	−7.7 ± 1.2[i]

[a] Ionic strength maintained at 1.00 M with NaClO$_4$ or KNO$_3$. [b] Results in the absence of added oxalate species. [c] Calculated at $\mu = 1.00\ M$, using data of ref 5 and 6. [d] $k_M = k_a' - k_1$, where k_a' is taken from Table IV. [e] $k_H = k_a + k_M = k_a + k_a' - k_1$, where k_a and k_a' are taken from Table IV. [f] Units are kcal/mol. [g] Units are cal/(mol deg). [h] Data of ref 6. [i] For k_H over all points, $\Delta H^\ddagger = 18.5 \pm 0.3$ kcal/mol and $\Delta S^\ddagger = -8.5 \pm 0.8$ eu.

entropy. The basic differences in the nature of activation parameters for k_M and k_H may signal fundamental differences in the detailed mechanisms of the two catalytic processes.

It is possible to rationalize the different observed rate laws for anation in sodium perchlorate and potassium nitrate with a single, steady-state reaction mechanism. The steps of this mechanism are given in eq 8 and 9. When the steady-state

$$cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- + H_2C_2O_4 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cr(C_2O_4)_2(HC_2O_4)(H_2O)^{2-} + H_3O^+ \tag{8}$$

$$Cr(C_2O_4)_2(HC_2O_4)(H_2O)^{2-} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Cr(C_2O_4)_3^{3-} + H_3O^+ \tag{9}$$

condition is assumed for the concentration of the $Cr(C_2O_4)_2(HC_2O_4)(H_2O)^{2-}$ complex intermediate, a closed-form rate law may be derived for the equilibration process which has an observed rate constant given by eq 10. In the event that $(k_2/k_3)[H^+] \gg 1$, eq 10 then reverts to eq 11. Equation

$$k_{obsd} = \frac{k_1[H_2C_2O_4] + k_4(k_2/k_3)[H^+]}{1 + (k_2/k_3)[H^+]} \tag{10}$$

$$k_{obsd} = (k_1k_3/k_2K_1)[HC_2O_4^-] + k_4[H^+] \tag{11}$$

10 is identical with eq 3, the form observed for k_s in potassium nitrate between 35 and 55°C. Equation 11 is the form of k_s which is observed in sodium perchlorate between 40 and 55°C. In the latter case, the derived anation rate constant, k_b of Table V, would be equal to k_1k_3/k_2K_1. The strength of this correlation is seen in the virtual identity of the activation energy of k_1k_3/k_2 computed for both media. In sodium perchlorate, k_bK_1 has an activation energy of 21.9 ± 0.2 kcal/mol; and, in potassium nitrate, k_1k_3/k_2 has an activation energy of 22.4 ± 0.4 kcal/mol.

We therefore conclude that the major difference in the anation mechanism for the two media lies in the magnitude of k_2/k_3. This parameter, which describes the tendency of the monodentate oxalate complex to aquate (k_2) vs. its tendency to chelate (k_3), must be larger in sodium perchlorate than it is in potassium nitrate. Since k_4 in sodium perchlorate is almost half the magnitude of k_4 in potassium nitrate, a simple and consistent rationalization of the difference in magnitude of k_2/k_3 would be provided if k_3 in sodium perchlorate were also half the magnitude of k_3 in potassium nitrate.[21]

The origin of the difference in magnitude of k_4, and the assumed difference in k_3, in the two media is somewhat obscure. Substitution of nitrate for perchlorate leads to a linear increase in the observed rate constant for the anation equilibration process. However, inclusion of a nitrate concentration term in the rate law for the equilibration process in potassium nitrate, alone, is unnecessary. Since activation enthalpies for k_4 are 21.6 kcal/mol in sodium perchlorate[10] and 21.9 ± 0.4 kcal/mol in potassium nitrate, the difference in rates manifests itself through minor differences in the activation entropy terms (−8.6 eu in NaClO$_4$ vs. −6.5 eu in KNO$_3$). Frank and Huchital[22] have noted a similar nitrate effect upon the trans–cis isomerization of $Cr(C_3H_2O_4)_2(H_2O)_2^-$, where complete dissociation of one end of a malonate ligand is implicated.

Direct nitrate involvement in the aquation of $Cr(C_2O_4)_3^{3-}$ seems unlikely in view of the data of Guastalla and Swaddle.[23] They have presented evidence for coordinated nitrate catalysis of the aquation of aquoamminechromium(III) complexes. Acceleration factors of 19–330 were determined, dependent upon the number and arrangement of aquo ligands in the chromium(III) coordination sphere. Nitrate catalysis was not evident for $Cr(NH_3)_6^{3+}$, which lacks an aquo ligand.

Entry of a bidentate oxalate ligand into the coordination sphere of chromium(III) defined by k_1k_3/k_2 is more rapid than the rate of exchange of the aquo ligands of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$.[14] Furthermore, k_1, which defines the rate of entry of a monodentate hydrogen oxalate ligand into the coordination sphere, is more than 200 times greater than the first-order rate constant for exchange of a single water molecule. These observations require a different detailed mechanism for anation than is provided by a simple dissociative mechanism involving an aquo ligand. It should be noted that k_1 is closely limited at all temperatures by the rate constant for the hydrogen ion catalyzed isomerization of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$. It is therefore conceivable that the activated complex or activating step for anation bears a strong resemblance to that for isomerization.

We feel that activation to anation involves attack by oxalic acid at a carboxylate site, protonation and partial dissociation of the carboxylate group, and entry of the hydrogen oxalate fragment into the coordination sphere at this site. These activating steps would then be followed by rapid displacement of H_3O^+ and chelation of one of the two hydrogen oxalate ligands which result from the activating step. The activation parameters determined for k_1 tend to support this conclusion. The activation enthalpy of k_1 is 2.2 kcal/mol greater and the activation entropy 7 cal/(mol deg) greater than the corresponding parameters for k_H. Since water apparently does not enter the coordination sphere of chromium(III) during the hydrogen ion catalyzed isomerization,[14] both increases would be necessary to cause entry of $HC_2O_4^-$ at a carboxylate site and ultimate displacement of an aquo ligand.

The failure of oxalic acid to affect the rate of the trans–cis isomerization is reasonable in terms of this mechanism if geometry changes during the anation step, k_1, and the aquation step, k_2, mirror each other—i.e., the processes occur either with no change in gross complex geometry or with opposing changes in geometry. In either case, the interaction of steps specified by k_1 and k_2 would produce no appreciable isomerization of the trans complex in the time scale of the observed isomerization reaction. Although the net effect of the interplay of processes defined by k_1, k_2, and k_3 is a formation rate for $Cr(C_2O_4)_3^{3-}$ which is almost 100 times slower than isomerization, attack of oxalic acid upon *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ should lead to an accelerated rate of water exchange, which is in turn limited by the isomerization rate.

The temperature dependence of the ratio k_2/k_3 specifies an activation energy for the aquation rate constant, k_2, which is 1.1 ± 0.1 kcal/mol greater than that of the chelation rate constant, k_3. Since k_2 is much greater in absolute magnitude than k_3, it is probable that k_2 also has a higher activation entropy. The activation enthalpy for the initiating aquation step, k_4, is also 1 kcal/mol greater than that for the anation initiating rate constant, k_1. However, the activation entropy is lower by 4.5 cal(mole deg). The differences in activation energies or enthalpies are consistent with our assignment of steps as "aquation" or "anation" steps. Differences in activation entropies are consistent with a situation in which all processes have similar intermediates prior to the rate-determining step.

Kelm and Harris have determined activation energies of 22.3 kcal/mol for anation of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ by the hydrogen oxalate and oxalate ions.[8] This value compares very favorably with the activation energies determined for the oxalic acid anation parameter, k_1k_3/k_2, in sodium perchlorate and potassium nitrate media. They have proposed an ion-pairing mechanism, contrary to our observations of the oxalic acid reaction, to justify observed rate constants of the form $k_{obsd} = k_wK[L]/(1 + K[L])$, where L is the hydrogen oxalate or oxalate ion. At 50°C and an ionic strength of 1.00 M, $k_w = 3.6 \times 10^{-3}$ sec^{-1}, $K = 0.85$ M^{-1} for the hydrogen oxalate ion, and $K = 1.8$ M^{-1} for the oxalate ion. We propose the following, alternate, steady-state mechanism to bring a degree of similarity to the seemingly different systems

$$cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- \underset{k_6}{\overset{k_5}{\rightleftarrows}} A; \quad d[A]/dt = 0 \tag{12}$$

$$A + L \xrightarrow{k_7} Cr(C_2O_4)_2(L)(H_2O)^- + H_2O \tag{13}$$

$$Cr(C_2O_4)_2(L)(H_2O)^- \xrightarrow{\text{very fast}} Cr(C_2O_4)_3^{3-} + H_2O \tag{14}$$

Our mechanism identifies k_w as k_5 and K as k_7/k_6. In the context of our mechanism, the parameter K describes the fate of intermediate A in the presence of $HC_2O_4^-$ or $C_2O_4^{2-}$ and has magnitudes which are consistent with the need for attack by an unprotonated carboxylate group of the entering ligand. The rate constant k_5 is similar in magnitude to that for the uncatalyzed isomerization of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ ($k_{H_2O} = 3.12 \times 10^{-3}$ sec^{-1} at 50°C and $\mu = 1.00$ M) and there is a strong possibility that uncatalyzed isomerization and anation share activating processes. In this case, the activation enthalpy of k_5 should approach 17.9 ± 0.5 kcal/mol. Kelm and Harris[8] have effectively determined the activation energy of $k_5(k_7/k_6)$, so no vertification of this point has been made.

We suggest that intermediate A contains two different forms of bidentate oxalate—one which is coordinated to chromium through an oxygen atom of each of the two carboxylate groups (oxalato-*O,O'*) and one which is coordinated through two oxygen atoms which exist on the same carboxylate group (oxalato-*O,O*). Anation would then be effected by attack of an unprotonated entering ligand at the oxalato-*O,O* site.

A similar intermediate could lead to uncatalyzed isomerization of the *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ complex ion or, upon protonation, could result in hydrogen ion catalyzed isomerization. If hydrogen ion catalysis is considered to be the simple consequence of a proton stabilizing the active oxalato-*O,O* ligand and thereby increasing the effective intermediate concentration, an acid dissociation constant of 0.108 M may be computed for the protonated form from the rate constant ratio k_{H_2O}/k_H at 50°C. This value is only slightly higher than the determined dissociation constant for oxalic acid at 50°C and is a factor of 10 larger than that measured for $Co(NH_3)_5(HC_2O_4)^{2+}$ [24] which contains the true monodentate ligand.

The protonated oxalato-*O,O* ligand conformation may also be implicated in the initiation of aquation of $Cr(C_2O_4)_3^{3-}$, in which case differences in the activation parameters of the isomerization, anation, and aquation processes would be determined by the hydrogen ion independent rate-determining step peculiar to each process. Activation parameters are similar because of the more labile nature of the (oxalato-*O,O*) ligand and are differentiated by the special requirements placed upon the process by the entering ligand and/or by specific geometry changes.

The protonated (oxalato-*O,O*) ligand has been proposed to explain hydrogen ion catalysis of ethylenediamine aquation for the $Cr(C_2O_4)_2(NH_2CH_2CH_2NH_2)^-$ complex.[16] Indeed, this ligand conformation may be central to explaining the similarity in reactivity of all oxalatochromate(III) complex species.

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Registry No. *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$, 18954-99-9; *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$, 15489-30-2; $H_2C_2O_4$, 144-62-7.

References and Notes

(1) G. E. Cunningham, R. W. Burley, and M. T. Friend, *Nature* (*London*), **169**, 1103 (1952).
(2) R. E. Hamm, *J. Am. Chem. Soc.*, **75**, 609 (1953).
(3) H. L. Schlafer, H. Gaussmann, and W. Tausch, *Z. Phys. Chem.* (*Frankfurt am Main*), **34**, 113 (1962).
(4) K. R. Ashley and R. E. Hamm, *Inorg. Chem.*, **4**, 1120 (1965).
(5) H. Kelm, H. Stieger, and G. M. Harris, *Ber. Bunsenges. Phys. Chem.*, **73**, 939 (1969).
(6) H. Kelm, H. Stieger, and G. M. Harris, *Z. Phys. Chem.* (*Frankfurt am Main*), **67**, 98 (1969).
(7) R. E. Hamm and R. E. Davis, *J. Am. Chem. Soc.*, **75**, 3085 (1953).
(8) H. Kelm and G. M. Harris, *Inorg. Chem.*, **6**, 706 (1967).
(9) K. V. Krishnamurty and G. M. Harris, *J. Phys. Chem.*, **64**, 346 (1960).
(10) D. Banerjea and M. S. Mohan, *J. Inorg. Nucl. Chem.*, **27**, 1643 (1965).
(11) H. Kelm and G. M. Harris, *Inorg. Chem.*, **6**, 1743 (1967).
(12) If aquation data are corrected for a slow, following step, Hammett plots indicate the need for only a first-order, hydrogen ion dependent term: C. A. Bunton, J. H. Carter, D. R. Llewellyn, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 4622 (1964).
(13) J. Aggett, I. Mawston, A. L. Odell, and B. E. Smith, *J. Chem. Soc. A*, 1413 (1968).
(14) H. Stieger, G. M. Harris, and H. Kelm, *Ber. Bunsenges, Phys. Chem.*, **74**, 262 (1970).
(15) A. Werner, *Justus Liebigs Ann. Chem.*, **406**, 216 (1914).
(16) T. W. Kallen, *Inorg. Chem.*, **14**, 2687 (1975).
(17) E. G. Moorhead and N. Sutin, *Inorg. Chem.*, **5**, 1866 (1966).
(18) R. F. Bauer and W. Mac F. Smith, *Can. J. Chem.*, **43**, 2755 (1965).
(19) K. R. Ashley and R. E. Hamm, *Inorg. Chem.*, **5**, 1645 (1966).
(20) [Cis]/[trans] = 20, from H. Kelm and G. M. Harris, *Z. Phys. Chem.* (*Frankfurt am Main*), **66**, 8 (1969). [Trans]/[cis] = 0.17, from M. W. Rophael and M. A. Malati, *J. Chem. Soc. A*, 1903 (1971).
(21) This simple expedient has the added virtue of maintaining the equilibrium constants k_1/k_2 and k_3/k_4 at the same magnitude in both KNO_3 and $NaClO_4$.
(22) M. J. Frank and D. H. Huchital, *Inorg. Chem.*, **11**, 776 (1972).
(23) G. Guastalla and T. W. Swaddle, *Inorg. Chem.*, **13**, 61 (1974).
(24) C. Andrade and H. Taube, *Inorg. Chem.*, **5**, 1087 (1966).