the above, the empirical form of the rate law is

$$d[V(V)]/dt = k[Am(V)][V(IV)] \qquad (5)$$

From the variation of the second-order rate parameter with change in temperature the values calculated by a nonlinear least-squares adjustment of the data with the Eyring formalism resulted in values of $\Delta H^* = 12.7 \pm 0.3$ kcal/mol and $\Delta S^* = -12.7 \pm 1.0$ cal deg^{-1} mol^{-1}. The empirical formula of the activated complex for the title reaction is one molecule of Am(V) and one of V(IV). The absence of any discernible hydrogen ion dependence on the rate of the reaction may well be a fortuitous cancellation of the expected positive hydrogen ion dependence for the transformation of the dioxoamericium(V) and the inverse dependence to be expected in the formation of V(V) from V(IV). Alternatively, the absence of a hydrogen ion dependent term in the rate law could be interpreted in a reaction scheme where an oxygen of the linear $O-Am-O^+$ replaces the water molecule trans to the "yl" oxygen of the V(IV)[12] with subsequent atom transfer.

Consistency between the demonstrated stoichiometry and the empirical form of the rate law requires that the rate of reaction 2 must be greater than that of the reaction

$$Am(IV) + Am(IV) \rightleftarrows Am(V) + Am(III) \qquad (6)$$

Since the second-order rate parameter for the latter reaction[3] is 5×10^6 M^{-1} s^{-1}, it is apparent that the former reaction must proceed at near the diffusion-controlled limit.

Previous studies of the oxidation of V(IV) by cations in aqueous perchlorate media in which the empirical form of the rate law has a major or sole term independent of hydrogen ion have been reported for Mn(III)[13] and Np(VII)[5] as oxidants. The respective reduction potentials (volts) for the Np(VII)/(VI), Mn(III)/(II), and Am(V)/(IV) couples are 2.0, 1.5, and 1.3. There is a parallel between the decrease in these potentials and the values of ΔG^* for the oxidation reactions (kcal/mol) of 13.3, 14.5, and 16.5, respectively. The respective enthalpies of activation also show parallel behavior with values (kcal/mol) of 6.7 ± 0.9, 11.1 ± 0.7, and 12.7 ± 0.3. The values of the entropies of activation, however, do not provide any obvious correlations with the other rate parameters or the potential values.

Registry No. AmO_2^+, 22878-02-0; VO^{2+}, 20644-97-7.

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Kinetics and Mechanism of Aquation of the *trans*-Bis(nitrilotriacetato-*N,O,O'*)chromate(III) Ion

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Received September 15, 1978

The *trans*-bis(nitrilotriacetato-*N,O,O'*)chromate(III) ion, *trans*-$Cr(NTA)_2^{3-}$, aquates in phthalate buffers to equilibrium mixtures of diaqua(nitrilotriacetato-*N,O,O',O''*)chromium(III), $Cr(NTA)(H_2O)_2$, and the (nitrilotriacetato-*N,O,O',O''*)(phthalato-*O,O'*)chromate(III) ion, $Cr(NTA)(phthalate)^{2-}$, in the pH range 1.50–6.00. The equilibrium constant for the formation of the $Cr(NTA)(phthalate)^{2-}$ ion from $Cr(NTA)(H_2O)_2$ and the phthalate ion was determined as $K_f = (1.6 \pm 0.2) \times 10^3$ M^{-1} at 25.0 °C and an ionic strength of 1.00 M. The kinetics of the single observed reaction step of this process was studied under pseudo-first-order conditions from pH 0.50 to pH 5.00 in phthalate buffers at four temperatures from 15.0 to 30.0 °C at an ionic strength of 1.00 M. The pseudo-first-order rate constant k_{obsd} was determined to be of the form given by $k_{obsd} = \{k_1 + k_4K_1[H^+] + k_5K_1K_2[H^+]^2 + k_HK_1K_2[H^+]^3\}/\{1 + K_1[H^+] + K_1K_2[H^+]^2\}$. The individual kinetics parameters of this expression were determined by a computer curve-fitting process at each temperature. Rate constants at 25.0 °C (s^{-1}), activation enthalpies (kcal mol^{-1}), and activation entropies (cal mol^{-1} K^{-1}) are as follows: k_1, 1.28×10^{-4}, 14.3 ± 0.6, -28.4 ± 2.2; k_4, 6.26×10^{-3}, 14.7 ± 0.1, -19.4 ± 0.3; k_5, 3.06×10^{-3}, 14.8 ± 0.7, -20.3 ± 2.3; k_H, 1.66×10^{-2} M^{-1} s^{-1}, 16.5 ± 0.8, -11.4 ± 2.6. Enthalpy changes associated with K_1 and K_2 were 1.6 ± 0.2 and -1.6 ± 0.4 kcal mol^{-1}. Entropy changes associated with K_1 and K_2 were 20.0 ± 0.7 and 3.3 ± 1.2 cal mol^{-1} K^{-1}. K_1 and K_2 have been interpreted as equilibrium constants for the protonation of the free carboxylate groups of *trans*-$Cr(NTA)_2^{3-}$, while k_1, k_4 and k_5 represent rate constants for the dissociation reactions of *trans*-$Cr(NTA)_2^{3-}$ and its two protonated forms, *trans*-$Cr(NTA)(HNTA)^{2-}$ and *trans*-$Cr(HNTA)_2^-$. The rate constant k_H was assigned to a hydrogen-ion-catalyzed steady-state dissociation process of *trans*-$Cr(HNTA)_2^-$. The observed rate law and kinetic parameters have been interpreted in terms of a mechanism where dissociation of a complete nitrilotriacetato-*N,O,O'* ligand is limited by dissociation at its nitrogen chromophore. An activation mechanism which includes a critical proton-transfer step has been proposed to explain the influence of protonated carboxylate groups on the rate of dissociation at the nitrogen chromophore.

Introduction

During the first observed step in the aquation of *cis*-$Cr(IDA)_2^-$ to $Cr(IDA)(H_2O)_3^+$ and *trans*-$Cr(MIDA)_2^-$ to $Cr(MIDA)(H_2O)_3^+$, the nitrogen chromophore of an IDA or MIDA ligand is replaced by an aqua ligand via hydrogen-ion-dependent pathways.[1,2] Simple amines and substituted amines generally undergo aquation through hydrogen-ion-independent pathways. Therefore it was proposed that dissociation and protonation of a carboxylate group of the ligand undergoing replacement preceded dissociation of the nitrogen

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chromophore in a two-step steady-state process.[2] Measurements of the carboxylate oxygen ^{18}O exchange rate of *trans*-Cr(MIDA)$_2^-$ tend to support such a proposal. All oxygen atoms exchange with solvent oxygen at the same rate in a manner consistent with rapid dissociation and rechelation of the coordinated carboxylate groups.[3]

The first step in the aquation of the glycinato-*N,O* ligand of Cr(ox)$_2$(gly)$^{2-}$ has also been shown to be displacement of coordinated nitrogen via a hydrogen-ion-dependent pathway.[4] In this case, the source of the observed hydrogen ion dependence was proposed to be protonation of an oxalato-*O,O′* ligand and proton transfer to the dissociating amine terminus of the glycinato-*N,O* ligand. "Intramolecular" proton transfer of this sort may be proposed to occur during the aquation of the nitrogen chromophores of *cis*-Cr(IDA)$_2^-$ and *trans*-Cr(MIDA)$_2^-$ as well, although the aquation kinetics data do not directly require such a step.

It is difficult to prove the existence of a critical, activating proton-transfer step in the nitrogen chromophore aquation mechanism of these complex ions by direct means. The low level of basicity or the need for dissociation of a coordinated carboxylate group of Cr(ox)$_2$(gly)$^{2-}$, *cis*-Cr(IDA)$_2^-$, or *trans*-Cr(MIDA)$_2^-$ must tend to limit the rate of aquation at the nitrogen chromophore by any "intramolecular" proton-transfer mechanism. However, kinetics data for the aquation of simple ethylenediamine[5,6] and polyamine[7–10] complexes of chromium(III) indirectly suggest active participation of protonated carboxylate groups in the general nitrogen chromophore aquation mechanism. In the absence of a protonated, vicinal carboxylate group, nitrogen chromophore aquation is slower by a factor of at least 10^3 at 25 °C, requires larger activation enthalpies, and proceeds with more positive activation entropies.

We have studied the aquation reaction of the *trans*-Cr(NTA)$_2^{3-}$ complex[11,12] to circumvent the restrictions placed upon possible intramolecular proton-transfer processes by coordination of associated carboxylate groups. This complex contains two free carboxylate groups which may participate in the aquation mechanism without first undergoing a rate-limiting dissociation step. Therefore, kinetics parameters for its aquation processes should more directly describe the relative importance of proton-transfer pathways.

Experimental Section

The *trans*-Cr(NTA)$_2^{3-}$ complex ion has been isolated by others as an ammonium salt by reaction of nitrilotriacetic acid with chromic hydroxide and ammonia.[11,12] We have devised a rapid, alternate method of preparation of the potassium salt of the complex ion which uses simple starting materials and has typical yields of 50–55%. This method uses an internal glycine/glycinate buffer to avoid precipitation or coprecipitation of insoluble polymeric species. A mixture of 26.7 g (0.10 mol) of green chromic chloride, 38.2 g (0.20 mol) of nitrilotriacetic acid, and 22.5 g (0.30 mol) of glycine in 150 mL of water was first heated to 90 °C. Next, 27.6 g (0.20 mol) of potassium carbonate was added in small portions and the solution was heated for 30 min at 90–95 °C to reduce its volume to 200 mL. Three separate 6.9-g (0.05 mol) portions of potassium carbonate were added at 30-min intervals while the solution was maintained at 90 °C and a volume of 200 mL. Following the last addition of potassium carbonate, the solution was heated for 45 min at 90–95 °C to reduce its volume to a point of incipient precipitation of the complex salt. The solution was finally insulated from its surroundings and was allowed to cool slowly to room temperature. The resulting crystalline solid was collected by filtration, washed with 50% ethanol, air-dried, stirred in acetone, filtered, and air-dried a second time. The final product was a pink crystalline material which showed little contamination by potassium chloride. Anal. Calcd for $K_3[Cr(C_6H_6NO_6)_2]\cdot 2H_2O$: Cr, 8.94; N, 4.82; K, 20.17; H_2O, 6.19. Found: Cr, 8.91 ± 0.02; N, 4.89 ± 0.04; K, 20.44 ± 0.09; H_2O, 6.53 ± 0.10. Chromium and nitrogen determinations have been described elsewhere.[13] Potassium was determined by a flame emission spectrophotometric technique and water was estimated as the mass loss of a 1-g sample of the complex salt at 90 °C.

The visible absorption spectrum of the complex salt was essentially identical with the spectrum described by Uehara et al.[12] The absorbance at the absorption maxima obeys Beer's law in the concentration range 0.004–0.020 M in unbuffered solutions. At 5 °C we found maxima at 356 nm (ϵ 31.8 ± 0.2 M^{-1} cm^{-1}) and 499 nm (ϵ 47.7 ± 0.2 M^{-1} cm^{-1}).

Pseudo-first-order rate constants for the displacement of one nitrilotriacetato ligand of *trans*-Cr(NTA)$_2^{3-}$ were determined spectrophotometrically at 572 nm with a Gilford Model 240 spectrophotometer. The temperature of the cell compartment was maintained within 0.05 °C of the desired value with a Lauda K2/R circulating constant-temperature bath. Each reaction was initiated by adding sufficient solid $K_3[Cr(NTA)_2]\cdot 2H_2O$ to 25.0 mL of temperature-equilibrated reactant solution to obtain a complex ion concentration of 3×10^{-3} or 6×10^{-3} M. After the complex salt had completely dissolved, a portion of the solution was transferred to a 1-cm cuvette in the spectrophotometer cell compartment, and the absorbance change accompanying the reaction was followed to within 5% of completion. Each reaction rate constant was determined as $-2.303m$, where m represents the slope of a conventional first-order semilog plot of $(A_\infty - A)$ vs. time for that reaction. Each reported rate constant is the average of duplicate determinations and is precise to within ±2%.

Solutions were prepared for the rate determinations at 0.5 pH unit intervals from pH 0.50 to pH 5.00. Solutions at pH 0.50 and pH 1.00 were unbuffered mixtures of standard perchloric acid and sodium perchlorate. Solutions between pH 1.50 and pH 5.00 were buffered by the phthalic acid/hydrogen phthalate/phthalate buffer system and were adjusted to the desired ionic strength with sodium perchlorate. Phthalate species were added as twice-recrystallized sodium hydrogen phthalate which had been dried to constant mass at 110 °C. The desired buffer composition was calculated by using $K_{a1} = 2.14 \times 10^{-3}$ M and $K_{a2} = 1.86 \times 10^{-5}$ M for phthalic acid at each temperature[14] and was obtained by adding calculated quantities of standard perchloric acid or sodium hydroxide. The total buffer concentration was fixed at 0.100 F except for those cases where solubility set a lower limit.

Solutions of the nitrilotriacetate displacement reaction product were intense purple in perchloric acid at pH 0.50 and pH 1.00 and in phthalate buffers from pH 1.50 to pH 2.50. In the absence of supporting electrolyte (μ = 0.05–0.32 M) the product complex was not retained by Dowex 50W-X8 (K^+ form) cation-exchange resin or by Dowex 1-X8 (Cl^- form) anion-exchange resin and was assumed to be Cr(NTA)(H_2O)$_2$. Intense blue solutions were obtained in the presence of a phthalate buffer at pH values above 3.00. At pH 5.00 and μ = 0.25 M the reaction product was retained by Dowex 1-X8 (Cl^- form) anion-exchange resin. It was not possible to elute this complex ion without its decomposition to Cr(NTA)(H_2O)$_2$. However, 0.50 M potassium chloride solution was sufficient to begin the elution process. Our experience indicates that ion-exchange behavior of this nature is representative of a relatively labile, dinegative complex ion.[4] The pH range of this study is lower than pK_{a1} and pK_{a2} for the aqua ligands of Cr(NTA)(H_2O)$_2$,[15] and the blue complex ion could not be Cr(NTA)(OH)(H_2O)$^-$ or Cr(NTA)(OH)$_2^{2-}$. Therefore we have designated its formula as Cr(NTA)(phthalate)$^{2-}$.

The equilibrium between the diaqua and phthalato complexes was studied by measuring the absorbance of solutions of the *trans*-Cr(NTA)$_2^{3-}$ complex after its reaction in perchloric acid and in phthalate buffer solutions at an ionic strength of 1.00 M. Initial *trans*-Cr(NTA)$_2^{3-}$ concentrations were maintained at 3.00×10^{-3} M, buffer concentrations were 0.025 and 0.100 F, temperature was maintained at 25.0 °C, and solution absorbance was measured at 400 and 540 nm. Absorbance measurements were made at times calculated to be equal to 10 and 15 half-lives of the aquation reaction. Results of these studies are shown in Figure 1 as plots of apparent molar absorptivity vs. solution pH for the two buffer formalities.

Visible absorption spectra of the reactant and product species involved in this study are shown in Figure 2. The spectra of Cr(NTA)(H_2O)$_2$ and Cr(NTA)(phthalate)$^{2-}$ were deduced from the limiting cases of the product equilibrium study. The visible absorption maxima of Cr(NTA)(H_2O)$_2$ are at 405 nm (ϵ 108.0 ± 1.0 M^{-1} cm^{-1}) and 555 nm (ϵ 103.5 ± 1.0 M^{-1} cm^{-1}) in a 0.025 F phthalate buffer at pH 1.50. The visible absorption maxima of Cr(NTA)(phthalate)$^{2-}$ are at 407 nm (ϵ 90.7 ± 1.0 M^{-1} cm^{-1}) and 573 (ϵ 95.5 ± 0.8 M^{-1} cm^{-1}) in a 0.100 F phthalate buffer at pH 6.00.

Results

The visible absorption spectra of *trans*-Cr(NTA)$_2^{3-}$ and

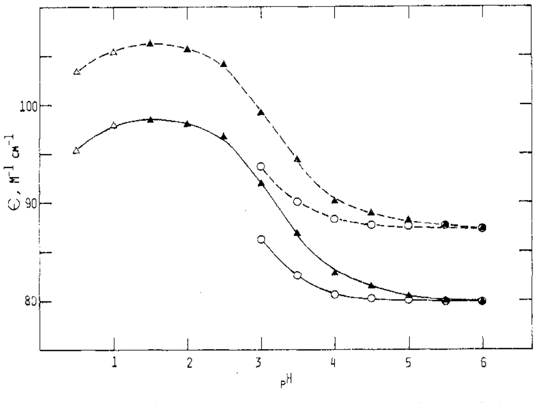


Figure 1. Variation of the apparent molar absorptivity of the *trans*-$Cr(NTA)_2^{3-}$ aquation product with pH and phthalate buffer formality at 400 (---) and 540 nm (—): (△) unbuffered solutions; (▲) phthalate buffer formality 0.025 F; (○) phthalate buffer formality 0.100 F.

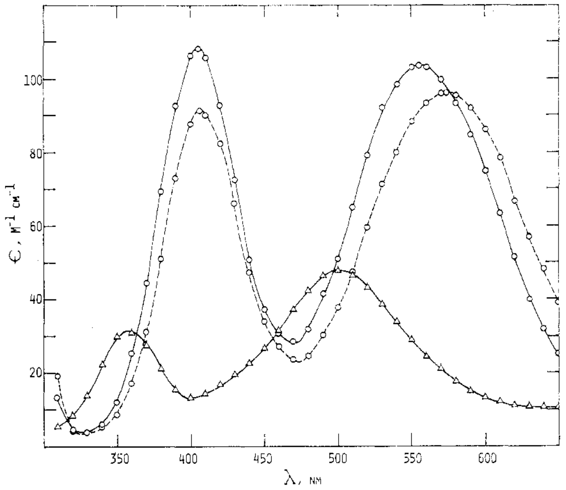


Figure 2. Visible and near-ultraviolet absorption spectra of *trans*-$Cr(NTA)_2^{3-}$ in pure water at 5.0 °C (-△-), $Cr(NTA)(H_2O)_2$ in a 0.025 F phthalate buffer at pH 1.50 and 25.0 °C (-○-), and $Cr(NTA)(phthalate)^{2-}$ in a 0.100 F phthalate buffer at pH 6.00 and 25.0 °C (--○--).

trans-$Cr(MIDA)_2^-$[16] are similar in all respects. Therefore it is probable that each nitrilotriacetato ligand of *trans*-$Cr(NTA)_2^{3-}$ is tridentate and possesses a single free carboxylate group. Weyh and Hamm[16] have suggested that the methyliminodiacetato-*N,O,O′* ligands of *trans*-$Cr(MIDA)_2^-$ occupy opposite faces of the coordination octahedron. The nitrilotriacetato-*N,O,O′* ligands of *trans*-$Cr(NTA)_2^{3-}$ should assume the same geometric arrangement.

The *trans*-$Cr(NTA)_2^{3-}$ complex ion aquates to $Cr(NTA)(H_2O)_2$ in the pH range of our kinetics study (eq 1).

$$trans\text{-}Cr(NTA)_2^{3-} + 2H_3O^+ \rightarrow Cr(NTA)(H_2O)_2 + H_2NTA^- \quad (1)$$

In contrast to its parent, this product has solution properties which are consistent with tetradentate coordination of the nitrilotriacetato ligand: (1) only two aqua protons of $Cr(NTA)(H_2O)_2$ may be titrated with strong base;[15] (2) the molar absorptivities at the absorption maxima of $Cr(NTA)(H_2O)_2$ are unusually large when compared with the structurally analogous tridentate ligand complexes $Cr(IDA)(H_2O)_3^+$ and $Cr(MIDA)(H_2O)_3^+$;[16] and (3) acidic solutions of $Cr(NTA)(H_2O)_2$ are not retained by cation exchange resins as complexes of a protonated, tridentate nitrilotriacetato-*N,O,O′* ligand would be. The spectral data of Figure 1 indicate a slight tendency for $Cr(NTA)(H_2O)_2$ to undergo partial aquation at very low pH values. Equilibrium quantities of the tridentate ligand complex $Cr(HNTA)(H_2O)_3^+$ may exist in this pH region.

Visible absorption spectra of the reaction product retain their relatively high molar absorptivities when conditions are varied, but the location of the complex ion's low-energy absorption maximum shifts to higher wavelengths as the pH or the phthalate buffer formality is increased. The observed spectral shift is reasonable if the primary reaction product exists in equilibrium with the bidentate phthalato-*O,O′* complex $Cr(NTA)(phthalate)^{2-}$ in the phthalate buffers of this study (eq 2 and 3). The relatively high molar absorptivity of the

$$Cr(NTA)(H_2O)_2 + C_6H_4(CO_2)_2^{2-} \overset{K_f}{\rightleftharpoons} Cr(NTA)(phthalate)^{2-} + 2H_2O \quad (2)$$

$$K_f = [Cr(NTA)(phthalate)^{2-}]/[Cr(NTA)(H_2O)_2] \times [C_6H_4(CO_2)_2^{2-}] \quad (3)$$

phthalato complex is consistent with tetradentate coordination of the nitrilotriacetato ligand and bidentate coordination of the phthalato ligand.[12,17]

The manner in which the absorbance of the product species at 400 and 540 nm varies with pH and phthalate buffer formality (Figure 1) may be correlated directly to the equilibrium of eq 2. If it is assumed that the apparent molar absorptivities found at the extremes of the pH variation of Figure 1 represent the molar absorptivities of pure $Cr(NTA)(H_2O)_2$ (ϵ_1 106.3 $M^{-1}\,cm^{-1}$ at 400 nm and ϵ_1 98.4 $M^{-1}\,cm^{-1}$ at 540 nm in a 0.025 F phthalate buffer at pH 1.50) and pure $Cr(NTA)(phthalate)^{2-}$ (ϵ_2 87.4 $M^{-1}\,cm^{-1}$ at 400 nm and ϵ_2 79.9 $M^{-1}\,cm^{-1}$ at 540 nm in a 0.100 F phthalate buffer at pH 6.00), then eq

$$K_f = (\epsilon_1 - \epsilon)([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})/(\epsilon - \epsilon_2)K_{a1}K_{a2}F_p \quad (4)$$

4 may be used to calculate the formation constant of the phthalato complex, K_f, given values of the apparent molar absorptivity, ϵ, at intermediate pH values. F_p of eq 4 represents the equilibrium formality of the phthalate buffer and K_{a1} and K_{a2} are the acid-dissociation constants of phthalic acid.[14] We have calculated $K_f = (1.6 \pm 0.2) \times 10^3\ M^{-1}$ from measurements of ϵ made in 0.025 and 0.100 F phthalate buffers in the pH range 2.50–5.00.

When all structural features of the reactant and product species are considered, the reaction of *trans*-$Cr(NTA)_2^{3-}$ in acidic solution must be described as the dissociation of a single nitrilotriacetato-*N,O,O′* ligand through a minimum of three steps, chelation of a free carboxylate group of the second ligand, and, in the case of reactions in phthalate buffers, establishment of the equilibrium of eq 2.

Despite the anticipated complexity of the reaction system, only a single step was observed for the conversion of *trans*-$Cr(NTA)_2^{3-}$ to $Cr(NTA)_2(H_2O)_2$ or equilibrium mixtures of $Cr(NTA)(H_2O)_2$ and $Cr(NTA)(phthalate)^{2-}$. Repetitive scans of the reaction system in a phthalate buffer at pH 5.00 are isosbestic with the product spectrum at 368, 461, and 507 nm through at least 95% of the reaction.

We have studied the kinetics of the observed reaction from pH 0.50 to pH 5.00 in phthalate buffers at temperatures of 15.0, 20.0, 25.0, and 30.0 °C. Ionic strength was maintained at 1.00 M with sodium perchlorate in all cases. Analytic phthalate concentrations were maintained at 0.100 F from pH 3.00 to pH 5.00. At lower pH values analytic phthalate formalities were reduced to 0.050 or 0.025 F as solubility dictated. Rate determinations at 25.0 °C and pH values from 1.50 to 2.50 indicated no dependence of the observed rate constant on the phthalate buffer formality. Average values of the observed rate constants at each set of reaction conditions are given in Table I.

Table I. Pseudo-First-Order Rate Constants for the Aquation Reaction of *trans*-Cr(NTA)$_2^{3-}$ in Sodium Perchlorate Media[a]

	$10^4 k_{\text{obsd}}$, s^{-1}			
pH	15.0 °C	20.0 °C	25.0 °C	30.0 °C
5.00[b]	0.902	1.40	2.22	3.47
4.50[b]	1.67	2.69	4.37	6.84
4.00[b]	3.68	6.12	9.93	15.5
3.50[b]	8.13	13.4	20.9	32.7
3.00[b]	15.0	25.1	39.5	64.3
2.50[c,d]	20.0[d]	31.1[d]	49.7[c,d]	78.1[c]
2.00[c,d]	19.6[d]	31.1[d]	49.0[c,d]	76.3[c]
1.50[c,d]	17.5[d]	27.5[d]	43.4[c,d]	70.2[c]
1.00[e]	19.7	32.4	49.2	79.1
0.50[e]	30.8	51.4	82.1	128

[a] Ionic strength 1.00 M; values are the average of duplicate determinations. [b] 0.100 F phthalate buffer; [*trans*-Cr(NTA)$_2^{3-}$]$_i$ = 6.0×10^{-3} M. [d] 0.025 F phthalate buffer; [*trans*-Cr(NTA)$_2^{3-}$]$_i$ = 3.0×10^{-3} M. [e] Unbuffered solution; [*trans*-Cr(NTA)$_2^{3-}$]$_i$ = 6.0×10^{-3} M.

We have closely described the complex pH dependence of k_{obsd} illustrated in Figure 3 by fitting the observed rate constants at each temperature to the general form of eq 5. A direct grid search which applied the least-squares judging criterion of eq 6 over all i data points was used to determine

$$k_{\text{obsd}} = \frac{a_1 + a_2[\text{H}^+] + a_3[\text{H}^+]^2 + a_4[\text{H}^+]^3}{1 + a_5[\text{H}^+] + a_6[\text{H}^+]^2} \tag{5}$$

$$S = \sum_i \{[f(a_j,[\text{H}^+]_i) - (k_{\text{obsd}})_i]/(k_{\text{obsd}})_i\}^2 \tag{6}$$

the fitting parameters, $a_j = a_1, ..., a_6$. Initial estimates of the a_j values were continuously varied until changes of 0.1% produced no decrease in S. This fitting program converged to the same set of three significant figure parameters (Table II) despite factor of 10 changes in the initial estimates.

Statistical test indicates that an acceptable fit has been determined by our fitting method. Values of $\chi^2 = S/(f(a_j,[\text{H}^+]_i)$ computed for each fit are significantly smaller than the critical χ^2 for rejection of the fit at the 95% confidence level.

The standard deviation of each fitting parameter, σ_j, has been estimated by Bevington's method[18] (eq 7 and 8). Each

$$\sigma_j = \Delta a_j(\Delta\chi^2)^{-1/2} \tag{7}$$

$$\Delta\chi^2 = \left(\chi_{a_j+\Delta a_j}{}^2 + \chi_{a_j-\Delta a_j}{}^2 - 2\chi_{a_j}{}^2\right)/2 \tag{8}$$

parameter of the final set was varied independently until a particular variation Δa_j produced an average change in χ^2 ($\Delta\chi^2$ of eq 8) of one unit. The value of Δa_j necessary to produce this change is in principle equal to σ_j. Standard deviations of the individual fitting parameters and χ^2 for each fit are given in Table II.

The kinetics data may also be fit to an equation formed by adding a third-order hydrogen-ion-dependent term to the denominator of eq 5. However, the quality of the fit is not improved by this modification. Simpler functions which lack the third-order hydrogen-ion-dependence term in the numerator or the second-order term in the denominator fail to fit the shallow minimum observed near pH 1.50.

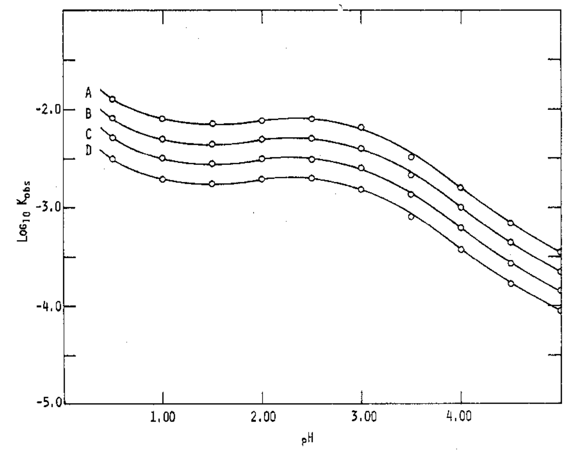


Figure 3. Variation of the observed rate constant for the aquation of *trans*-Cr(NTA)$_2^{3-}$ with pH at (A) 30.0, (B) 25.0, (C)20.0, and (D) 15.0 °C. Ionic strength 1.00 M (NaClO$_4$).

Discussion

Although the large absorbance increase accompanying the reaction of *trans*-Cr(NTA)$_2^{3-}$ must be due to conversion of a tridentate nitrilotriacetato-*N,O,O′* ligand to its strained, asymmetric, tetradentate nitrilotriacetato-*N,O,O′,O″* bonding configuration, coordination of a free carboxylate group cannot be rate determining to the observed reaction. Sykes and coworkers[19] have recently demonstrated that the free carboxylate group of the pentadentate EDTA complex Cr(EDTA)(H$_2$O)$^-$ labilizes the sixth chromium(III) coordination position to substitution via extremely rapid coordination and dissociation steps. The free carboxylate group of one nitrilotriacetato-*N,O,O′* ligand of *trans*-Cr(NTA)$_2^{3-}$ may rapidly displace a coordinated carboxylate group of the other by a similar mechanism; however, complete dissociation of the resulting nitrilotriacetato-*N,O* ligand must be limited by the relatively slow dissociation reaction of its inaccessible nitrogen chromophore and two reaction steps would be observed. Since we have observed only one reaction step, it is much more likely that coordination of a free carboxylate group follows or occurs in concert with dissociation of the nitrogen chromophore.

Scheme I illustrates one of several conceivable sequences of equilibria and rate-determining steps that are at least superficially consistent with the kinetics data. Within this scheme, K_1 and K_2 are represented as equilibrium constants for stepwise protonation of the two free carboxylate groups of *trans*-Cr(NTA)$_2^{3-}$. The rate constants k_1, k_4, and k_5 define the nitrogen chromophore dissociation rate of the *trans*-Cr(NTA)$_2^{3-}$, *trans*-Cr(NTA)(HNTA)$^{2-}$, and *trans*-Cr(HNTA)$_2^-$ complex ions, respectively; and the rate constant k_6 defines the hydrogen-ion-catalyzed aquation rate of a coordinated

Table II. Hydrogen Ion Concentration Dependence Curve-Fitting Parameters for the Aquation Reaction of *trans*-Cr(NTA)$_2^{3-}$ in Sodium Perchlorate Media[a,b]

parameter	15.0 °C	20.0 °C	25.0 °C	30.0 °C
$10^5 a_1$	5.586 ± 0.029[c]	8.091 ± 0.097[c]	12.84 ± 0.12[c]	20.06 ± 0.27[c]
a_2	3.656 ± 0.016	6.219 ± 0.048	10.05 ± 0.07	15.79 ± 0.16
$10^{-2} a_3$	1.579 ± 0.084	2.438 ± 0.132	3.618 ± 0.380	6.136 ± 0.769
$10^{-2} a_4$	6.800 ± 0.064	12.18 ± 1.24	19.62 ± 2.78	30.07 ± 5.52
$10^{-3} a_5$	1.430 ± 0.038	1.534 ± 0.058	1.605 ± 0.064	1.639 ± 0.077
$10^{-5} a_6$	1.200 ± 0.043	1.201 ± 0.043	1.184 ± 0.077	1.207 ± 0.100
χ^2 [d]	6.043	1.652	5.940	2.795

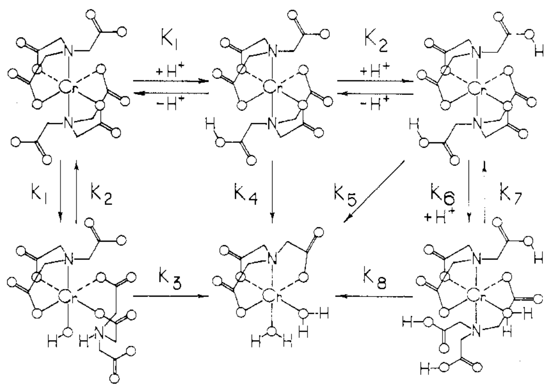
[a] Derived by fitting k_{obsd} of Table I to the expression $k_{\text{obsd}} = (a_1 + a_2[\text{H}^+] + a_3[\text{H}^+]^2 + a_4[\text{H}^+]^3)/(1 + a_5[\text{H}^+] + a_6[\text{H}^+]^2)$. [b] Ionic strength 1.00 M. [c] Standard deviation. [d] $\chi^2 > 9.488$ for rejection of fit at 95% confidence level for four degrees of freedom.

Table III. Derived Rate Constants for the Aquation Reaction of *trans*-$Cr(NTA)_2^{3-}$ in Sodium Perchlorate Media[a]

parameter[b]	15.0 °C	20.0 °C	25.0 °C	30.0 °C
$10^5 k_1$, s^{-1}	5.59 ± 0.03[c]	8.09 ± 0.10[c]	12.8 ± 0.1[c]	20.1 ± 0.3[c]
$10^3 k_4$, s^{-1}	2.56 ± 0.07	4.05 ± 0.16	6.26 ± 0.25	9.63 ± 0.46
$10^3 k_5$, s^{-1}	1.32 ± 0.08	2.03 ± 0.13	3.06 ± 0.38	5.08 ± 0.76
$10^3 k_H$, M^{-1} s^{-1}	5.67 ± 0.57	10.1 ± 1.1	16.6 ± 2.6	24.9 ± 5.0
$10^{-3} K_1$, M^{-1}	1.43 ± 0.04	1.53 ± 0.06	1.60 ± 0.06	1.64 ± 0.08
$10^{-1} K_2$, M^{-1}	8.39 ± 0.37	7.83 ± 0.41	7.38 ± 0.56	7.36 ± 0.70

[a] Derived from the data of Table II; ionic strength 1.00 M. [b] $k_1 = a_1$, $k_4 = a_2/a_5$, $k_5 = a_3/a_6$, $k_H = a_4/a_6$, $K_1 = a_5$, and $K_2 = a_6/a_5$. [c] Standard deviation.

Scheme I



carboxylate group of *trans*-$Cr(HNTA)_2^-$.

When the aquation process is initiated by dissociation at the nitrogen chromophore, the labilizing influence of the second nitrilotriacetato-*N,O,O′* ligand upon adjacent carboxylate groups should cause complete dissociation (k_3 and analogous rate constants) to be more rapid than recoordination of the protonated nitrogen chromophore (k_2 and analogous rate constants). However, recoordination of a protonated carboxylate group (k_7) and dissociation at the nitrogen chromophore (k_8) are likely to have similar rates, and steady-state concentrations of $Cr(HNTA)(H_2NTA)(H_2O)$ may accumulate when the aquation process is initiated by carboxylate group aquation.

If it is considered that $k_3 >> k_2$ and the steady-state condition is placed on the concentration of $Cr(HNTA)(H_2NTA)(H_2O)$, Scheme I leads to the form of k_{obsd} given by eq 9 and 10. These equations in turn identify the

$$k_{obsd} = \frac{k_1 + k_4K_1[H^+] + k_5K_1K_2[H^+]^2 + k_HK_1K_2[H^+]^3}{1 + K_1[H^+] + K_1K_2[H^+]^2} \tag{9}$$

$$k_H = k_6k_8/(k_7 + k_8) \tag{10}$$

curve-fitting parameters of eq 5 as $a_1 = k_1$, $a_2 = k_4K_1$, $a_3 = k_5K_1K_2$, $a_4 = k_HK_1K_2$, $a_5 = K_1$, and $a_6 = K_1K_2$. Values of the individual rate and equilibrium constants of eq 9 have been derived from the curve-fitting parameters at each temperature and are given in Table III. The activation parameters and equilibrium thermodynamic parameters related to these constants are given in Table IV.

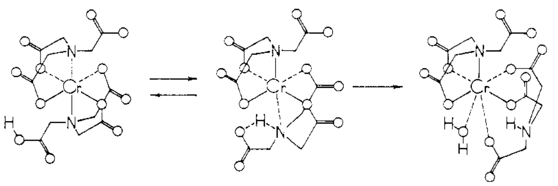
The curve-fitting process and the reaction sequence of Scheme I are validated in part by the standard deviations associated with the thermodynamic parameters of the derived rate and equilibrium constants. Standard deviations of ΔH and $\Delta H^‡$ values average ±0.6 kcal mol^{-1}, while standard deviations of ΔS and $\Delta S^‡$ values average ±1.8 cal mol^{-1} K^{-1}. Standard deviations of this magnitude must be considered extremely reasonable for parameters derived from such a complex rate law over a temperature interval of only 15 °C.

Table IV. Activation Parameters and Equilibrium Thermodynamic Parameters of the Derived Rate Constants for the Aquation Reaction of *trans*-$Cr(NTA)_2^{3-}$ [a]

parameter	$\Delta H^‡$, kcal mol^{-1}	$\Delta S^‡$, cal mol^{-1} K^{-1}
k_1	14.3 ± 0.6[b]	−28.4 ± 2.2[b]
k_4	14.7 ± 0.1	−19.4 ± 0.3
k_5	14.8 ± 0.7	−20.3 ± 2.3
k_H	16.5 ± 0.8	−11.4 ± 2.6
parameter	ΔH, kcal mol^{-1}	ΔS, cal mol^{-1} K^{-1}
K_1	1.6 ± 0.2[b]	20.0 ± 0.7[b]
K_2	−1.6 ± 0.4	3.3 ± 1.2

[a] Ionic strength 1.00 M ($NaClO_4$). [b] Standard deviation.

Scheme II



Values determined for the acid-association constants K_1 and K_2 tend to support their assignment to carboxylate group protonation equilibria in the reaction sequence of Scheme I. Their magnitudes (log K_1 = 3.18 and log K_2 = 1.89 at 20.0 °C) compare favorably with the reciprocals of the first and second acid-dissociation constants of nitrilotriacetic acid (−log K_{a1} = 1.99 and −log K_{a2} = 2.27 at 20 °C[20]) and with the reciprocal of the first acid-dissociation constant of $Cr(HEDTA)(H_2O)$ (−log K_{a1} = 2.27 at 18 °C[21]). The first protonation step of *trans*-$Cr(NTA)_2^{3-}$ appears to be influenced more strongly by the formal charge of the complex ion than does the second step.

Similarities in the activation enthalpies determined for k_1, k_4, and k_5 are consistent with their assignment to the analogous nitrogen chromophore dissociation steps of *trans*-$Cr(NTA)_2^{3-}$, *trans*-$Cr(NTA)(HNTA)^{2-}$, and *trans*-$Cr(HNTA)_2^-$. In addition, relationships between the activation parameters of these rate constants shed light on at least three significant mechanistic details. First, stepwise protonation of the free carboxylate groups of *trans*-$Cr(NTA)_2^{3-}$ does little to alter the activation enthalpy of the nitrogen chromophore dissociation process. The protonated species react more rapidly than *trans*-$Cr(NTA)_2^{3-}$ due to increased activation entropies for their dissociation steps. Second, the activation entropy of the nitrogen chromophore dissociation step remains at a relatively large negative value despite protonation of the free carboxylate groups of the complex ion. Finally, the entropy decrease which accompanies activation of the nitrogen chromophore dissociation steps of *trans*-$Cr(NTA)(HNTA)^{2-}$ and *trans*-$Cr(HNTA)_2^-$ is almost identical with the entropy increase that occurs when one or both free carboxylate groups of *trans*-$Cr(NTA)_2^{3-}$ are protonated.

The entropy relationships between k_4, k_5, K_1, and K_2 are consistent with the detailed activation mechanism of Scheme II. Scheme II illustrates an activation mechanism in which proton transfer from a protonated carboxylate group to the departing nitrogen chromophore is critical to acceleration of the dissociation process. The activation entropy associated with

Table V. Kinetics Parameters for the Nitrogen Chromophore Dissociation Process of a Series of Related Chromium(III) Complex Species

complex	rate law term	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}	$10^3 k_{25}$°C
trans-$Cr(NTA)_2^{3-}$ [a]	k_1	14.3	−28.4	0.128^{d}
trans-$Cr(NTA)(HNTA)^{2-}$ [a]	k_4	14.7	−19.4	6.26^{d}
trans-$Cr(HNTA)_2^{-}$ [a]	k_5	14.8	−20.3	3.06^{d}
trans-$Cr(HNTA)_2^{-}$ [a]	$k_H[H^+]$	16.5	−11.4	16.6^{e}
trans-$Cr(MIDA)_2^{-}$ [b]	$k'[H^+]$	17.0	−18.6	0.188^{e}
	$k''[H^+]^2$	15.6	−21.2	0.574^{f}
cis-$Cr(IDA)_2^{1-}$ [b]	$k'[H^+]$	15.3	−17.0	7.08^{e}
$Cr(ox)_2(gly)^{2-}$ [c]	k''	17.6	−18.6	0.08^{d}
	$k'[H^+]$	17.0	−14.5	1.57^{e}

[a] This study; ionic strength 1.00 M ($NaClO_4$). [b] Ionic strength 0.9 M ($NaClO_4$).[2] [c] Ionic strength 1.0 M ($NaClO_4$).[4] [d] In s^{-1}. [e] In M^{-1} s^{-1}. [f] In M^{-2} s^{-1};

a dissociation process of this nature should be negative as we have observed. The protonated carboxylate group must certainly attain a specific ordered conformation to affect proton transfer. In addition, two new ionic sites are created by proton transfer. Electrostrictive effects about these sites would create additional order among solvent molecules in their vicinity. If the proton transfer is complete during the activating step, the sum of these negative contributions to the activation entropy may well equal the entropy increase that occurs when an ionic carboxylate group is protonated.

The activation enthalpy for dissociation of a nitrogen chromophore of *trans*-$Cr(NTA)_2^{3-}$ is substantially lower than ΔH^{*} for aquation of simple ethylenediamine[5] and polyethylenepolyamine[7–10] complexes of chromium(III). Furthermore, stepwise protonation of the free carboxylate groups of *trans*-$Cr(NTA)_2^{3-}$ fails to alter the activation enthalpy for the nitrogen chromophore dissociation process. These observations are mutually consistent if an ionic carboxylate group of *trans*-$Cr(NTA)_2^{3-}$ or the ionic carboxylate group resulting from the proton-transfer step of Scheme II partially stabilizes the vacated sixth coordination position of the activated complex. Aquation at the nitrogen chromophore of the nitrilotriacetato-*N,O,O′* ligand would then occur in a series of steps of low activation enthalpy and associative character. In the absence of a stabilizing vicinal carboxylate group, the activation enthalpy for nitrogen chromophore dissociation must be considerably more dissociative in character.

The second-order rate constant k_H has a somewhat greater activation enthalpy and entropy than k_1, k_4, or k_5. This is consistent with its assignment to a steady-state process initiated by hydrogen-ion-catalyzed dissociation of a coordinated carboxylate group of *trans*-$Cr(HNTA)_2^{-}$. Similar steady-state processes have been proposed to describe hydrogen-ion-catalyzed aquation of a nitrogen chromophore of *trans*-$Cr(MIDA)_2^{-}$,[2] *cis*-$Cr(IDA)_2^{-}$,[2] and $Cr(ox)_2(gly)^{2-}$,[4] and the kinetic parameters for these processes closely parallel those determined for k_H (Table V). *trans*-$Cr(NTA)_2^{3-}$ is the most reactive of this set of related complex ions. Relative reactivity via this steady-state pathway is largely determined by differences in activation entropy.

The existence of a critical proton-transfer step cannot be demonstrated directly when the nitrogen chromophore dissociation process is the final step of a steady-state process. For example, k_H is a composite constant given by $k_H = k_6k_8/(k_7 + k_8)$, and its activation parameters will only strongly reflect the activation parameters of k_8 when $k_7 >> k_8$. However, k_H and the second- and third-order aquation rate constants for *trans*-$Cr(MIDA)_2^{-}$, *cis*-$Cr(IDA)_2^{-}$, and $Cr(ox)_2(gly)^{2-}$ all possess the negative activation entropy and low activation enthalpy that we have been able to relate to a proton-transfer step. Therefore, there is a strong possibility that the mechanism of Scheme II generalizes to the nitrogen chromophore dissociation step of each of these complex species as well.

The *trans*-$Cr(NTA)_2^{3-}$ aquation sequence of Scheme I and the detailed proton-transfer mechanism of Scheme II must be considered speculative. However, the facility with which they may be used to describe and relate the aquation processes of *trans*-$Cr(NTA)_2^{3-}$ and related complex species requires that they be given serious consideration in the mechanistic studies of other aminopolyacetato complexes of chromium(III).

Registry No. $K_3[Cr(C_6H_6NO_6)_2]$, 71424-37-8; $Cr(NTA)(H_2O)_2$, 18042-08-5; $Cr(NTA)(phthalate)^{2-}$, 71382-13-3.

References and Notes

(1) Abbreviations used in this paper for coordinated ligands: gly^- = glycinate ion, $NH_2CH_2CO_2^-$; IDA^{2-} = iminodiacetate ion, $NH(CH_2CO_2)_2^{2-}$; MIDA = methyliminodiacetate ion, $CH_3N(CH_2CO_2)_2^{2-}$; NTA^{3-} = nitrilotriacetate ion, $N(CH_2CO_2)_3^{3-}$; $HNTA^{2-}$ = $HO_2CCH_2N(CH_2CO_2)_2^{2-}$; H_2NTA^- = $(HO_2CCH_2)_2NCH_2CO_2^-$; $EDTA^{4-}$ = ethylenediamine-*N,N,N′,N′*-tetraacetate ion, $(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2^{4-}$; ox^{2-} = oxalate ion, $C_2O_4^{2-}$.

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