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The Acid-Catalyzed Aquation of the α-Oxalatotriethylenetetraminechromium(III) Ion[1]

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The primary step in the aquation of α-Cr(trien)(C_2O_4)$^+$ has been found to be the formation of the previously unreported Cr(trienH)(OH_2)(C_2O_4)$^{2+}$, probably of the α configuration. The acid dependence of the observed pseudo-first-order rate constant can be empirically described by $k_{obsd} = (k_1K[H^+])/(1 + K[H^+])$. The value of k_1 is $(2.91 \pm 0.06) \times 10^{-4}$ sec^{-1} at 25.00 ± 0.02° and $\mu = 1.97$. The activation parameters for k_1 are $\Delta H^{\ddagger} = 19.9 \pm 0.6$ kcal mole^{-1}, $E_a = 20.5 \pm 0.6$ kcal mole^{-1}, and $\Delta S^{\ddagger} = -8.1 \pm 1.9$ cal deg^{-1} mole^{-1}.

Introduction

Historically much effort in coordination chemistry has focused on the kinetic and mechanistic behavior of octahedral disubstituted bis(ethylenediamine) complexes of Co(III) and, to a lesser extent, Cr(III). Attempts to systematize reaction patterns and parameters can benefit not only from comparisons between complexes differing only in the central metal atom but also from comparisons between analogous species differentiated by the complexity of chelation. In particular, interesting contrasts should arise when the chelation progresses from bidentate bis(ethylenediamine) to quadridentate triethylenetetramine which may be viewed as two ethylenediamine ligands linked by a bridging ethylene group. A series of such disubstituted triethylenetetraminechromium(III) complexes has recently been synthesized, including the compound of interest here, α-Cr(trien)(C_2O_4)$^+$.[2,3] This cation can theoretically exist as two geometric isomers (Figure 1) with the α form being the least sterically strained. House and Garner concluded that the Cr(trien)(C_2O_4)$^+$ ion has the α configuration.[2]

This paper describes the study of the kinetics of the primary aquation of α-Cr(trien)(C_2O_4)$^+$, the development of a mechanism to account for the acid dependence of the hydrolysis, and the characterization of the new complex Cr(trienH)(OH_2)(C_2O_4)$^{2+}$. This complex is presumed to be of the α form and results from the rupture of a primary Cr–N bond, followed by proton uptake, together with the coordination of a water molecule.

Experimental Section

α-Oxalatotriethylenetetraminechromium(III) Perchlorate Monohydrate.—This compound was synthesized by a modification of an earlier procedure.[2] The α-Cr(trien)(C_2O_4)$^+$ resulting from the reaction of $H_2C_2O_4 \cdot 2H_2O$, $Na_2Cr_2O_7$, and trien was precipitated as the bromide dihydrate and purified by recrystallization from aqueous $NaClO_4$ as the perchlorate monohydrate. Analysis showed $C_2O_4^{2-}$/Cr mole ratios of 0.989, 1.00, and 1.02. The infrared spectrum of the perchlorate salt was identical with that of an authentic sample provided by Dr. D. A. House. The visible absorption spectrum was in general agreement with the published spectrum,[2] except for differences apparently due to the slight aging of the solution used by House and Garner. Samples of α-[Cr(trien)(C_2O_4)]$ClO_4 \cdot H_2O$ stored in a desiccator at room temperature in the dark slowly deteriorated with time.

All subsequent preparations gave visible and infrared spectra in agreement with known samples and were further characterized by confirming the appearance of appropriate isosbestic points identical with those found during aquation of an authentic sample of α-Cr(trien)(C_2O_4)$^+$.

α-Oxalatoaquohydrogentriethylenetetraminechromium(III) Cation.—Samples of α-Cr(trien)(C_2O_4)$^+$ were aquated in 0.1 *F* HNO_3 at 20–25° for 2.5–3.5 hr followed by adsorption on a 2-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 cation-exchange resin (100–200 mesh). The column was washed with *ca.* 200 ml of 0.8 *F* HNO_3 to remove all traces of parent. The daughter was eluted with *ca.* 100 ml of 2.0 *F* HNO_3. It was characterized by $C_2O_4^{2-}$/Cr mole ratios, elution behavior, and chemical considerations, as discussed later. Attempts to prepare solid salts were unsuccessful.

Other Chemicals.—All other chemicals were CP or reagent grade. Water used was purified by ion-exchange resin.

Analytical Methods.—Chromium was determined by heating known volumes of the complex-ion solutions with alkaline H_2O_2, diluting to an appropriate volume, and determining the resultant CrO_4^{2-} at 372 mμ with a Beckman Model DU spectrophotometer.

Oxalate was found by titration of solutions *ca.* 2 *F* in $HClO_4$ with a 1 *N* solution of $H_2Ce(ClO_4)_6$ in 6 *M* $HClO_4$ to a nitroferroin end point.[4]

Kinetic Methods.—All kinetic measurements were based on spectrophotometric analysis. The reaction was not followed by cation-exchange chromatographic separation of parent and product since no combination of eluent strength and column length tried gave solutions of pure parent uncontaminated by daughter.

The low solubility (*ca.* 0.220 m*F*) of α-[Cr(trien)(C_2O_4)]$ClO_4 \cdot H_2O$ in 2 *F* $HClO_4$ precluded the convenient use of $HClO_4$ as reaction solvent. Instead, all runs were made in HNO_3 solutions with ionic strength adjusted with $LiNO_3$.

Spectrophotometric runs were made in matched 10.00-cm quartz cells using a Beckman Model DK-2 recording spectrophotometer equipped with a water-cooled lamphousing and a thermostated cell holder. Temperature accuracy was better than ±0.02°. All reaction times were accurate to ±0.01 min. During a run reaction solutions were exposed to no light other than that of the spectrophotometer beam. Previous work indicates that light of this intensity would have minimal catalytic effect. In a typical run *ca.* 14 mg of α-[Cr(trien)(C_2O_4)]$ClO_4 \cdot H_2O$ was dissolved in *ca.* 60 ml of solvent, previously equilibrated at the run temperature.

Tests for release of ligand $C_2O_4^{2-}$ were made by quenching a

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[1] Presented at the 22nd Annual Northwest Regional Meeting of the American Chemical Society, Richland, Wash., June 1967.

[2] D. A. House and C. S. Garner, *J. Am. Chem. Soc.*, **88**, 2156 (1966).

[3] Abbreviations used: en, ethylenediamine; trien, triethylenetetramine.

[4] G. Frederick Smith, "Cerate Oxidimetry," The G. Frederick Smith Chemical Co., Columbus, Ohio, 1964, p60.

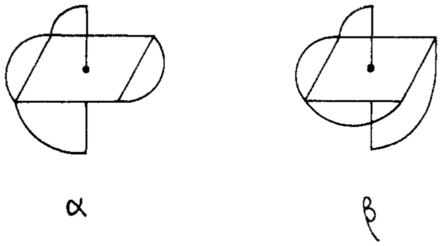

Figure 1.—Geometric isomers possible for an octahedral complex formed from symmetric quadridentate and symmetric bidentate ligands. For this paper the ligands are triethylenetetramine and oxalate, respectively.

10-ml aliquot in 25 ml of ice-cold H_2O and adsorbing the complex on a 10-cm × 1-cm diameter column of H^+ Dowex AG50WX-8 (100–200 mesh); the effluent plus 15 ml of 0.1 F $HClO_4$ column wash solution were collected and analyzed for $C_2O_4^{2-}$. Tests with known amounts of $C_2O_4^{2-}$ showed quantitative recovery of $C_2O_4^{2-}$. A blank was tested under identical conditions. The $C_2O_4^{2-}$ determination had to be run in $HClO_4$ rather than HNO_3 since NO_3^- adversely affected the titration.

Kinetic Calculations.—Kinetic data evaluation was carried out by digital computer. A FORTRAN program for calculating first-order rate constants, activation parameters, and extrapolation of rate constants to other temperatures was kindly provided by Wilkins and Klopfenstein.[5] This program was translated into ALGOL for use on a Burroughs B5500 computer. For rate constant calculations, the program was modified to accept experimental absorbancy values at given times and an independently calculated value of the infinite-time absorbancy. A subprogram was added that generated both kinetic and Arrhenius plots on a California Computer Products Model 565-570 plotter.

During a typical run, spectra were recorded up to an estimated 2 half-lives. The absorbancy *vs.* time values at a given wavelength and a calculated infinite-time absorbancy based on a known complex-ion concentration were submitted to the computer. The computer-drawn kinetic plot was examined and those values at long reaction times were discarded which clearly curved away from the very obvious straight line defined by the large number of experimental points. The remaining data were resubmitted to the computer until no further refinement was necessary (see Figure 3).

Table I

Absorption Maxima and Minima from 350 to 700 mμ at 20–25° in 2 F HNO_3[a]

Complex	λ_{max}, mμ	λ_{min}, mμ	λ_{max}, mμ
α-Cr(trien)$(C_2O_4)^+$	370 (104)	420 (33.7)	495 (147)
α-Cr(trienH)$(OH_2)(C_2O_4)^{2+}$	392 (63.2)	450 (20.0)	520 (63.2)

[a] Figures inside parentheses are molar absorbancy indices a_M in M^{-1} cm^{-1}.

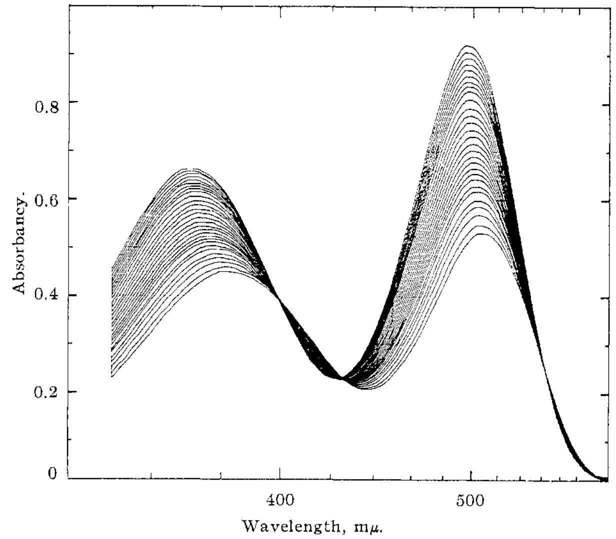

Figure 2.—Visible spectral changes during acid hydrolysis of 0.642 mF α-Cr(trien)$(C_2O_4)^+$ in 1.175 F HNO_3, μ = 1.98 at 25.00°. Spectra shown to *ca.* 1.4 half-lives. The upper trace on both peaks is the zero-time spectrum.

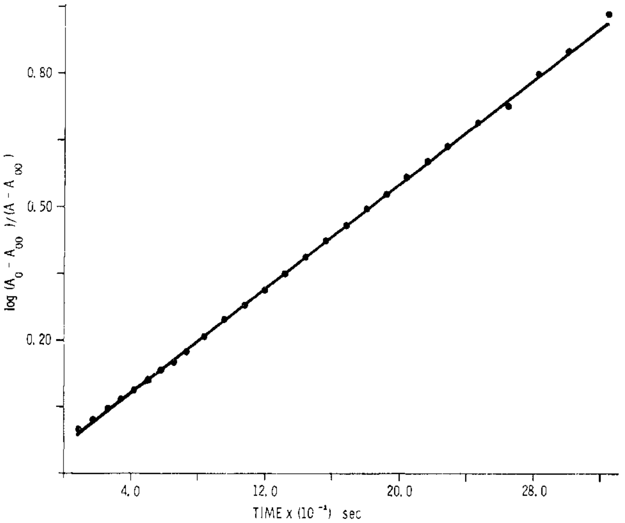

Figure 3.—Typical first-order rate plot for aquation of α-Cr(trien)$(C_2O_4)^+$ in 1.175 F HNO_3, μ = 1.98 at 25.00°.

Results

Visible Spectra of Complexes.—The minima, maxima, and molar absorbancy indices of the near-ultraviolet and visible absorption spectra of α-Cr(trien)$(C_2O_4)^+$ and α-Cr(trienH)$(OH_2)(C_2O_4)^{2+}$ are presented in Table I.

Rate of Aquation of α-Cr(trien)$(C_2O_4)^+$.—The hydrolysis of α-Cr(trien)$(C_2O_4)^+$ was followed spectrophotometrically. The data were analyzed by computer using the relationship

$$\ln [(A_0 - A_\infty)/(A - A_\infty)] = k_{obsd}t$$

where A_0 is the zero-time absorbance and assuming 100% aquation to α-Cr(trienH)$(OH_2)(C_2O_4)^{2+}$ for calculation of the infinite-time absorbance (A_∞). Pseudo-first-order kinetic plots containing 15–30 experimental points were linear to *ca.* 1.4 half-lives. Figure 2 illustrates a typical spectrophotometric run while Figure 3 shows a computer-drawn kinetic plot. Good agreement between rate constants were obtained for kinetic analyses at 360, 370, 475, and 500 mμ. The most accurate rate constants were found at 500 mμ where there is maximum difference between molar absorbancy values for parent and daughter (*ca.* 94 M^{-1} cm^{-1}). All rate constants quoted are for this wavelength and have been assigned a ±2% limit of error based on experimental variation in the molar absorbancy indices for α-Cr(trienH)$(OH_2)(C_2O_4)^{2+}$.

The effect on the observed aquation rate of acid con-

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(5) C. L. Wilkins and C. E. Klopfenstein, *J. Chem. Educ.*, **43**, 10 (1966); also personal communication.

centration, ionic strength, complex-ion concentration, and temperature was studied. The kinetic data for the aquation are compiled in Table II.

TABLE II

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE AQUATION OF α-Cr(trien)(C_2O_4)$^+$

Temp, °C	(HNO_3), F	μ, F[a]	C_0, mF	10^4k_{obsd}, sec^{-1} [b]
15.00	2.03	2.03	0.619	0.89 ± 0.02
20.00	1.99	1.99	0.603	1.65 ± 0.03
25.00	1.96	1.96	0.606	2.89 ± 0.06
25.00	1.99	2.99	0.606	2.56 ± 0.05
25.00	1.98	1.98	0.266	2.90 ± 0.06
30.00	1.99	1.99	0.637	5.25 ± 0.10
25.00	1.87[c]	1.87	0.220	2.63 ± 0.05
25.00	1.18	1.98	0.642	2.93 ± 0.06
25.00	0.98	0.98	0.543	3.10 ± 0.06
25.00	0.60	0.60	0.648	3.56 ± 0.07
25.00	0.57	1.97	0.565	2.77 ± 0.05
25.00	0.57	0.97	0.572	3.20 ± 0.06
25.00	0.29	1.99	0.552	2.59 ± 0.05
25.00	0.10	0.10	0.640	3.63 ± 0.07
25.00	0.095	2.00	0.533	2.40 ± 0.05
25.00	0.112	2.00	0.588	2.41 ± 0.05

[a] Ionic strength adjusted with $LiNO_3$. [b] Assumed ±2% limit of error. [c] $HClO_4$ used instead of HNO_3. C_0 here is near-solubility limit. Despite filtration of the reaction mixture, some undissolved complex may have been present.

Discussion

The primary step in the hydrolysis of α-Cr(trien)(C_2O_4)$^+$ could conceivably involve a reaction at any one of three distinctly different ligand–metal bond sites—a primary nitrogen of the triethylenetetramine, a secondary nitrogen of the same ligand, or the oxalate. Space-filling molecular models suggest the unlikelihood of a secondary nitrogen–chromium bond rupture leading to product formation since there are steric restrictions that would prevent the then uncoordinated segment of the trien from moving far enough away from the metal to allow the coordination of an incoming water molecule.

Other evidence not only indicates the improbability of oxalate release but also supports the conclusion that the most likely reaction site is a primary Cr–N bond. Were a half-bonded oxalate formed as the first step in the aquation of α-Cr(trien)(C_2O_4)$^+$, the total release of oxalate from the complex would presumably follow. However, when a solution of α-Cr(trien)(C_2O_4)$^+$ was aquated at 25° for 30 hr (*ca.* 45 half-lives for primary aquation and *ca.* 18 half-lives for secondary hydrolysis), a test for free oxalate on the solution chromatographically separated from all Cr(III) species showed <1% free oxalate. Cation-exchange chromatography of a similar solution after *ca.* 5 half-lives clearly showed the presence of only a single primary hydrolysis product; this ion had a ligand oxalate to chromium mole ratio of 0.93. Furthermore, the visible absorption spectrum of a solution of α-Cr(trien)(C_2O_4)$^+$ aged for 1 month in the dark at 20–25° agreed closely with that of the very stable $Cr(OH_2)_4(C_2O_4)^+$ in the location of wavelength maxima and minimum, as well as molar absorbancy indices.[6] In an investigation of a related system Schläfer found that the acid hydrolysis of Cr(en)(C_2O_4)$_2^-$ proceeded by release of ethylenediamine rather than oxalate.[7] Similarly, Garner and Hsu have reported that a stepwise displacement of trien occurs during hydrolysis of β-Cr(trien)(OH_2)Cl^{2+}.[8] Evidence from less directly related systems has shown that release of amine ligands prior to hydrolysis of acido ligands appears to be a characteristic of many Cr(III) systems.[9–14]

In near-ultraviolet and visible spectral regions a shift toward longer wavelengths occurs as the reaction progresses (Figure 2). Though such behavior can sometimes be employed to differentiate between possible reaction pathways in light of the relative positions of the ligands in the spectrochemical series, it appears that the stepwise displacement of either an amine ligand or a coordinated oxalate leads to similar spectral changes. The release of trien from β-Cr(trien)(OH_2)Cl^{2+} shows a displacement toward longer wavelength[8] as does the loss of en from Cr(en)(C_2O_4)$_2^-$, $Cr(en)_2(OH_2)_2^{3+}$, and $Cr(en)_3^{3+}$.[7,15] A similar shift would be seen during stepwise oxalate hydrolysis because the unidentate oxalate ligand has a lower position in the spectrochemical series than does bidentate oxalate.[16]

An over-all reaction scheme consistent with the assumption that the aquation proceeds *via* a primary Cr–N bond fission shows α-Cr(trienH)(OH_2)(C_2O_4)$^{2+}$ as the single product. The characterization of the daughter depends on the evidence already cited, as well as the acid dependence discussed below. In addition, the expected dipositive nature of the product was confirmed by cation-exchange chromatography which showed that the elution behavior of the ion was characteristic of known dipositive complexes of similar size.[9–11,13]

The single pathway for the disappearance of α-Cr(trien)(C_2O_4)$^+$ is substantiated by (1) the appearance of only one product during cation-exchange resin chromatography of aged reaction solutions, (2) the linearity of the pseudo-first-order rate plot to at least 1.4 half-lives where the infinite-time absorbancy value used to determine the rate constant was calculated from the zero-time spectrum of chromatographically separated α-Cr(trienH)(OH_2)(C_2O_4)$^{2+}$, and (3) the three experimentally observed isosbestic points which are

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(6) G. M. Harris, personal communication. Also D. Banerjea and M. S. Mohan, *J. Inorg. Nucl. Chem.*, **26**, 613 (1964); H. L. Schläfer and W. Tausch in "Essays in Coordination Chemistry," W. Schneider, G. Anderegg, and R. Gut, Ed., Birkhäuser Verlag, Basel, 1964, p 189.

(7) H. L. Schläfer, *J. Inorg. Nucl. Chem.*, **13**, 101 (1960).

(8) C. Y. Hsu and C. S. Garner, *Inorg. Chim. Acta*, **1**, 17 (1967).

(9) C. S. Garner and D. J. MacDonald in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, pp 266–275.

(10) D. J. MacDonald and C. S. Garner, *J. Am. Chem. Soc.*, **83**, 4152 (1961).

(11) D. J. MacDonald and C. S. Garner, *Inorg. Chem.*, **1**, 20 (1962).

(12) D. C. Olson and C. S. Garner, *ibid.*, **2**, 414 (1963).

(13) L. P. Quinn and C. S. Garner, *ibid.*, **3**, 1348 (1964).

(14) J. M. Veigel and C. S. Garner, *ibid.*, **4**, 1569 (1965).

(15) H. L. Schläfer and R. Kollrack, *Z. Physik. Chem.* (Frankfurt), **18**, 348 (1958); H. L. Schläfer and O. Kling, *ibid.*, **16**, 14 (1958).

(16) Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, **29**, 311 (1956).

maintained for at least 1 half-life and occur at 399 ± 1 mμ (a_M = 62 ± 4 M^{-1}c m^{-1}), 425 ± 2 mμ (a_M = 34 ± 2M^{-1} cm^{-1}), and 562 mμ (a_M = 40 ± 3 M^{-1} cm^{-1}). These values compare well with the isosbestic points generated by the spectra of the two pure components of 397 mμ (a_M = 63.5 M^{-1} cm^{-1}), 426 mμ (a_M = 35.1 M^{-1} cm^{-1}), and 555 mμ (a_M = 48.8 M^{-1} cm^{-1}) except at the highest wavelength where the large slope of the spectral curves limits accuracy. A fourth isosbestic point is possibly present at *ca.* 610 mμ, but the low values of the molar absorbancy indices in this range make definite identification difficult. While the agreement between calculated and experimental isosbestic points serves to confirm the chromatographic evidence for only a single product, it should be noted that the appearance of experimental isosbestic points unsupported by other evidence does not conclusively prove the number of products formed. This arises because, in addition to those isosbestic points which may occur in the familiar cases of a reactant giving a single product or two products formed in constant ratio, a system of three or more components may have isosbestic points with molar absorbancy indices unrelated to the molar absorbancy indices of the individual components.[17]

In the absence of oxalate hydrolysis the most satisfactory explanation for the increased ionic charge found in the product is the uptake of a proton by the trien ligand. The acid dependence thus suggested can be seen in Table II. In Figure 4 the dependence of the observed pseudo-first-order rate constant on acid concentration at μ = 1.98 ± 0.02 and 25.00° is illustrated. As is shown, k_{obsd} becomes acid independent above *ca.* 1 F HNO$_3$, while falling off in a nonlinear curve below that concentration. An empirical equation fitting the experimental acid dependence is

$$k_{\text{obsd}} = \frac{k_1K(\text{H}^+)}{1 + K(\text{H}^+)}$$

The physical interpretation of k_1 and the composite K is discussed below. When $K(\text{H}^+) \gg 1$ the expression reduces to $k_{\text{obsd}} = k_1$ while at low acid concentrations k_{obsd} should tend to zero. A mechanistic explanation of this behavior requires that the initial step be an equilibrium between α-Cr(trien)(C$_2$O$_4$)$^+$ and an intermediate resulting from the rupture of a primary Cr–N bond, followed by proton uptake by the basic, uncoordinated amine function of the trien. This mechanism is illustrated in Figure 5. Application of the steady-state approximation results in the expression given above for k_{obsd} where now K is k_3/k_2.

With the mechanism as written it is mathematically impossible to calculate values of k_2 and k_3 since no properties of the intermediate are known. The ratio k_3/k_2 reflects the fate of the intermediate since it shows the relative competition between product formation and a return to the parent. This ratio can be calculated, but possibly because of ionic activity variations at these high ionic strengths it does not have a constant value. The ratio in 0.57 F HNO$_3$ (μ = 1.97 at 25.00°) is 35, while in 1.98 F HNO$_3$ under otherwise identical conditions k_3/k_2 = 146. Though the rate of protonation has a diffusion-controlled upper limit, large departures from diffusion-controlled rates have been observed in the presence of intramolecular hydrogen bonding.[18] In this case it can be noted only that the rate of proton uptake by the free end of the trien is at least an order of magnitude faster than the reformation of the parent complex.

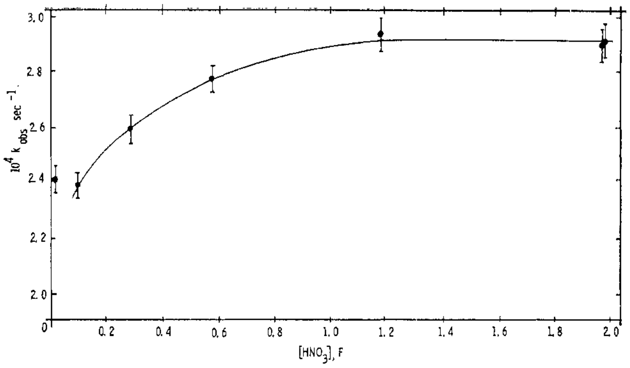

Figure 4.—Acid dependence of k_{obsd} at μ = 1.98 and 25.00° for hydrolysis of α-Cr(trien)(C$_2$O$_4$)$^+$.

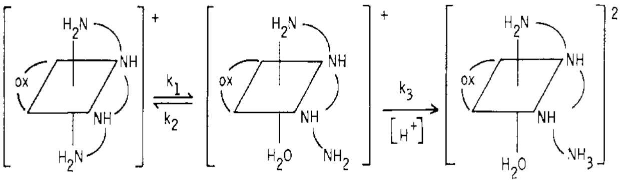

Figure 5.—Reaction mechanism for the acid-catalyzed aquation of α-Cr(trien)(C$_2$O$_4$)$^+$.

An alternative mechanism that also accounts for the observed acid dependence postulates an initial equilibrium between unreacted parent and a protonated but unhydrolyzed α-Cr(trien)(C$_2$O$_4$)$^+$. If the protonated complex aquates more rapidly than does unprotonated α-Cr(trien)(C$_2$O$_4$)$^+$, an acid-independent region would be observed at high acidity when the limiting concentration of protonated α-Cr(trien)(C$_2$O$_4$)$^+$ was reached. If such an equilibrium existed, there presumably would be an observable spectral difference between protonated and unprotonated α-Cr(trien)(C$_2$O$_4$)$^+$. Though no spectral difference was found whether the complex was dissolved in 0.095 F HNO$_3$ (μ = 2.00) or 2.00 F HNO$_3$, such protonations have been reported in strongly acid solutions, despite the lack of obvious bonding sites on the coordinated nitrogen.[19]

The data of Table II indicate that k_1 is essentially independent of initial complex-ion concentration over a 2.4-fold change in initial concentration of α-Cr(trien)(C$_2$O$_4$)$^+$. When the ionic strength is increased from 1.98 to 2.99 M with LiNO$_3$ at a constant acid concentration of 1.98 M, the value of k_1 decreased by *ca.* 12%,

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[17] C. F. Timberlake and P. Bridle, *Spectrochim. Acta*, **23A**, 313 (1967).

[18] L. D. Maeyer and K. Kustin, *Ann. Rev. Phys. Chem.*, **14**, 10 (1963); H. Strehlow, *ibid.*, **16**, 172 (1965).

[19] E. A. Healy and R. K. Murmann, *J. Am. Chem. Soc.*, **79**, 5827 (1957); **83**, 2092 (1961).

a not unexpected result at this high ionic strength. Figure 4 shows that in unbuffered 0.0095 *F* HNO_3 the observed rate constant has begun to rise, possibly indicative of the increasing competition from base hydrolysis at lower acid concentrations.

No conclusive identification of the isomeric nature of $Cr(trienH)(OH_2)(C_2O_4)^{2+}$ is possible particularly in the absence of a solid sample of the product. Only a single product was chromatographically isolated; yet one α and two β isomers are the theoretically possible aquated configurations (a *trans* product containing bidentate oxalate is an obvious impossibility). If β-$Cr(trienH)(OH_2)(C_2O_4)^{2+}$ were formed, it could arise either from a rapid isomerization of the parent to β-$Cr(trien)(C_2O_4)^+$ followed by the observed aquation or from the rapid isomerization of the directly formed α-$Cr(trienH)(OH_2)(C_2O_4)^{2+}$. In either case the isomerization would have to be rapid on the experimental time scale since neither α-$Cr(trien)(C_2O_4)^+$ nor $Cr(trienH)(OH_2)(C_2O_4)^{2+}$ showed any change in their respective visible spectra regardless of the age of the solutions when the complexes were chromatographically isolated, yet the possible isomers of each complex would be expected to have observably different spectra. No analogous systems seem to have been reported treating the isomerization of a polydentate amine ligand simultaneously undergoing stepwise acid hydrolysis. Compelling evidence against the possibility of any α–β isomerization exists in the already illustrated exceptional stability of the oxalate ligand, since certain isomerization pathways require movement of the oxalate. A pathway involving rearrangement of two trien bonds is also unlikely. Therefore isomeric retention in the product α-$Cr(trienH)(OH_2)(C_2O_4)^{2+}$ is presumed.

Because of the complex nature of the rate law, activation parameter calculations can be associated with a single reaction step only in the acid-independent region where the observed rate constant contains only k_1, the rate constant for the rupture of the primary nitrogen–chromium bond. Values of k_1 at $[H^+] = 1.99 \pm 0.04$ *M* ($\mu = 1.99$) at 15.00, 20.00, 25.00, and 30.00° were evaluated by computer. Errors were estimated by calculating the activation parameters for k_1 at its ±2% limit of error. The results are $\Delta H^{\ddagger} = 19.9 \pm 0.6$ kcal mole^{-1}, $E_a = 20.5 \pm 0.6$ kcal mole^{-1}, and $\Delta S^{\ddagger} = -8.1 \pm 1.9$ cal deg^{-1} mole^{-1}. An activation energy of this magnitude is typical of both Cr(III) and Co(III) systems. The negative entropy of activation may result from the hydrogen bonds formed between H_2O and the uncoordinated, as yet unprotonated, primary amine segment of the trien. This would serve to increase the order within the inner solvation sphere, decrease solvent to solvent shell interchange, restrict the mobility of the free one-fourth of the trien, and facilitate the coordination of the incoming water molecule.

Meaningful comparisons with analogous Co(III) and Cr(III) systems are not possible because of the dearth of published data. The complex $M(en)_2(C_2O_4)^+$, where M = Cr(III), has been synthesized,[20] but its reaction is only vaguely referred to as a "color change" after 1.5 hr at 30° in 0.1 *M* $ZnSO_4$.[21] When M = Co(III), the complex is unaffected by heating at 90° in 1 *M* HNO_3 for 1–2 hr.[22] This stability is inexplicable in view of the apparent hydrolysis of the Cr(III) analog,[21] as well as the aquation behavior reported here for α-$Cr(trien)(C_2O_4)^+$. The contrasts that might arise between α-$Cr(trien)(C_2O_4)^+$ and $Co(trien)(C_2O_4)^+$ would be of interest. Both the α and β isomers of the Co(III) complex have been prepared,[23] but the acid hydrolysis of neither ion has yet been reported.

A mechanism similar to that suggested here has previously been postulated for the hydrolysis of tris-(2,2′-dipyridyl)iron(II)[24] while structures containing "half-bonded" polyamine ligands have been utilized to explain the hydrolysis of β-$Cr(trien)(OH_2)Cl^{2+}$[8] as well as a number of complexes of Ni(II).[25]

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