Contribution from the Department of Chemistry,
The University of Chicago, Chicago, Illinois 60637

Preparation and Aquation Kinetics of the Pentaaquo(2-mercaptoethylammonium-*S*)chromium(III) Ion. Origin of the k_0 Term in Rate Laws of the Form $-\mathrm{d}(\ln [(\mathrm{H_2O})_5\mathrm{CrX}]^{n+})/\mathrm{d}t = k_0 + k_1(\mathrm{H^+})$

LEON E. ASHER and EDWARD DEUTSCH*

Received January 3, 1973

The $[(\mathrm{H_2O})_5\mathrm{CrSCH_2CH_2NH_3}]^{3+}$ ion has been prepared *via* chromium(II) reduction of the *N,S*-(2-mercaptoethylamine)bis(ethylenediamine)cobalt(III) ion in aqueous perchloric acid and subsequent ion exchange separation of the product mixture. In aqueous perchloric acid (0.01-1.99 *F*), this complex aquates according to the rate law $-\mathrm{d}(\ln [\mathrm{CrSR}]^{3+})/\mathrm{d}t = k_0 + k_1(\mathrm{H^+})$. At $\mu = 2.00$ *F* ($\mathrm{LiClO_4}$), 25°, the specific rate constants are $k_0 = (4.5 \pm 0.2) \times 10^{-5}\ \mathrm{sec^{-1}}$ and $k_1 = (1.31 \pm 0.02) \times 10^{-4}\ F^{-1}\ \mathrm{sec^{-1}}$. The corresponding activation parameters are $\Delta H_0^* = 27.6 \pm 0.4$ and $\Delta H_1^* = 20.6 \pm 0.3$ kcal/mol, and $\Delta S_0^* = 14.0 \pm 1.2$ and $\Delta S_1^* = -7.1 \pm 0.9$ eu. Data are correlated to show that for pentaaquochromium(III) complexes of ligands derived from weak acids, the k_0 and k_1 terms in the title rate law are similarly dependent upon the ability of the coordinated ligand to be protonated. This provides the first positive evidence that the k_0 term of these complexes describes separation of HX from $[(\mathrm{H_2O})_4(\mathrm{OH})\mathrm{Cr}]^{2+}$ and not X from $[(\mathrm{H_2O})_5\mathrm{Cr}]^{3+}$. It is also shown that the former k_0 mechanism operates when the $\mathrm{p}K_\mathrm{a}$ of HX is >2, while the latter k_0 mechanism operates when the $\mathrm{p}K_\mathrm{a}$ of HX is <0.

Introduction

In a previous paper[1] we studied the acid-catalyzed aquation of an arylthiolatochromium(III) complex and pointed out that in order to distinguish between possible origins of the k_0 term in the aquation rate law

$$-\mathrm{d}(\ln [(\mathrm{H_2O})_5\mathrm{CrSR}]^{n+})/\mathrm{d}t = k_\mathrm{obsd} = k_0 + k_1(\mathrm{H^+}) \tag{1}$$

it would be desirable to establish the dependence of k_0 on the Bronsted basicity of the coordinated sulfur. This may be accomplished *via* a detailed kinetic study of the aquation of an alkylthiolatochromium(III) complex, and accordingly this paper describes the preparation and aquation kinetics of the pentaaquo(2-mercaptoethylammonium-*S*)chromium(III) ion. In aqueous perchloric acid the net equation for this reaction is

$$\mathrm{H_3O^+} + (\mathrm{H_2O})_5\mathrm{CrSCH_2CH_2NH_3}^{3+} \rightarrow (\mathrm{H_2O})_6\mathrm{Cr}^{3+} + \mathrm{HSCH_2CH_2NH_3}^{+} \tag{2}$$

The results of this study have not only fulfilled the original goal but have also provided the impetus for us to correlate all available data concerning the acid-catalyzed aquation of $[(\mathrm{H_2O})_5\mathrm{CrX}]^{n+}$ complexes. This correlation provides the first direct evidence as to the origin of the k_0 aquation path for the species, $[(\mathrm{H_2O})_5\mathrm{CrX}]^{n+}$, where X is a ligand derived from a weak acid.

Experimental Section

Equipment. The instrumentation used to obtain pmr spectra, visible-ultraviolet spectra, pH measurements, and kinetic data was the same as previously described.[1] Computer calculations were also performed as previously described, the LASL nonlinear least-squares program again being used for all data analysis.[2] Polarographic studies employed a Beckman Electroscan 30 equipped with a dropping mercury electrode.

Materials. Common laboratory chemicals, water, perchloric acid, Dowex 50W-X2 ion exchange resin, lithium perchlorate, hexaaquochromium(III) perchlorate, and solutions of chromium(II) perchlorate were obtained and purified as previously described.[1,3] Cystamine (2,2′-dithiobis[ethylamine]) dihydrochloride, 2-mercaptoethylamine hydrochloride, and 2-mercaptoethanol were purchased from Aldrich Chemical Co. and used without further purification. Salts of the 4,4′-dithiobis(*N,N,N*-trimethylanilinium) cation were available from previous work.[1] The disulfide of trimethylmercaptomethylammonium perchlorate was prepared by a literature procedure.[4] *N,S*-(2-Mercaptoethylamine)bis(ethylenediamine)cobalt(III) perchlorate was prepared by the method of Lane and Bennett.[5] After precipitation from the reaction solution with excess perchloric acid, this complex was twice crystallized from water, washed with 95% ethanol, and air-dried. The visible-ultraviolet spectrum exhibits peaks at 280 (ϵ 1.35 × $10^3\ F^{-1}\ \mathrm{cm^{-1}}$) and 482 nm ($\epsilon$ 150 $F^{-1}\ \mathrm{cm^{-1}}$) with a shoulder at *ca.* 590 nm. The pmr spectrum in $\mathrm{D_2O}$ shows two complex multiplets, centered at approximately 100 and 60 Hz downfield from *tert*-butyl alcohol, with areas in a ratio of 5/1; this is consistent with one sulfur-bound and five nitrogen-bound $\mathrm{CH_2}$ groups. *Anal.* Calcd for $\mathrm{C_6H_{22}N_5SCo(ClO_4)_2}$: C, 15.89; H, 4.88; N, 15.42. Found: C, 15.94; H, 4.88; N, 15.59. Recrystallization from excess sodium iodide readily yielded the iodide salt. *Anal.* Calcd for $\mathrm{C_6H_{22}N_5SCoI_2}$: C, 14.16; H, 4.36; N, 13.76; S, 6.30; I, 49.85. Found: C, 14.12; H, 4.35; N, 13.48; S, 5.87; I. 49.20.

Preparation of Pentaaquo(2-mercaptoethylammonium-*S*)chromium(III) Solutions. Solutions of the $[(\mathrm{H_2O})_5\mathrm{CrSCH_2CH_2NH_3}]^{3+}$ ion were prepared by the chromium(II) reduction of *N,S*-(2-mercaptoethylamine)bis(ethylenediamine)cobalt(III) in aqueous perchloric acid and subsequent ion-exchange separation of the product mixture. In a typical preparation 3.3 mmol of the cobalt complex was dissolved in 100 ml of 2.4 *F* $\mathrm{HClO_4}$ and the solution was deoxygenated with a nitrogen stream and cooled in an ice bath (to retard aquation of the desired product). Chromium(II) perchlorate (2.6 ml of 1.3 *F* solution) was then added, reduction of cobalt(III) occurring within the time of mixing. The resulting green-brown solution was diluted to approximately 0.1 *F* ionic strength with chilled water and added to a Dowex 50W-X2 ion-exchange column approximately 30 cm long and 2.5 cm in diameter. After loading, elution was carried out with first 1 *F* and then 2 *F* $\mathrm{NaClO_4}$ (pH *ca.* 3) unless the ionic strength of the eluent would contribute more than 1% of the total ionic strength of planned kinetic experiments. In this case comparable $\mathrm{LiClO_4}$ solutions were used to elute the desired complex. Separation of the 3+ ions from $[\mathrm{Co_{aq}}]^{2+}$ and from higher charged polymeric species was easily effected by this procedure. However, the 3+ ions $[(\mathrm{H_2O})_5\mathrm{CrSCH_2CH_2NH_3}]^{3+}$ and $[(\mathrm{H_2O})_6\mathrm{Cr}]^{3+}$, its aquation product, were not completely differentiated; therefore the 3+ band was collected in successive 10-ml fractions and each fraction was spectrophotometrically monitored for the presence of the desired product. The ratio of the absorbance at 438 nm to that at 578 nm [1.77 for desired product *vs.* 0.68 for hexaaquochromium(III)] proved to be an excellent indicator of the relative concentration of these two species. The final solutions were usually about 0.02 *F* in chromium, of which less than 5% was $[(\mathrm{H_2O})_6\mathrm{Cr}]^{3+}$, the overall yield of $[(\mathrm{H_2O})_5\mathrm{CrSCH_2CH_2NH_3}]^{3+}$ being greater than 80%. All ion-exchange procedures were carried out in a cold room at 5°, and the final solutions were stored at −20° after rapid freezing in liquid nitrogen.

Analyses. Elemental analyses of solid compounds were performed by PCR, Inc., of Gainesville, Fla. Total perchlorate was determined as previously described.[1] The total chromium concentration of solutions was measured spectrophotometrically as chromate

---

(1) L. E. Asher and E. Deutsch, *Inorg. Chem.*, 11, 2927 (1972).

(2) R. H. Moore and R. K. Zeigler, Los Alamos Scientific Laboratory Report No. LA-2367, 1959, plus addenda.

(3) E. Deutsch and H. Taube, *Inorg. Chem.*, 7, 1532 (1968).

(4) H. Bohme and W. Schlephack, *Justus Liebigs Ann. Chem.*, 630, 105 (1960).

(5) R. H. Lane and L. E. Bennett, *J. Amer. Chem. Soc.*, 92, 1089 (1970).

Table I. First-Order Rate Constants for the Aquation of $[(H_2O)_5CrSCH_2CH_2NH_3]^{3+}$ as a Function of Temperature, Acid Concentration, and Ionic Strength ($LiClO_4$)

16.3°, $\mu = 2.00\ F$		25.0°, $\mu = 2.00\ F$		34.4°, $\mu = 2.00\ F$		44.3°, $\mu = 2.00\ F$		34.4°, $H^+ = 0.10\ F$		25.0°, $\mu = 1.00\ F$	
$[H^+]$, F	10^5k_{obsd}, sec^{-1}	$[H^+]$, F	10^5k_{obsd}, sec^{-1}	$[H^+]$, F	10^5k_{obsd}, sec^{-1}	$[H^+]$, F	10^5k_{obsd}, sec^{-1}	μ, F	10^5k_{obsd}, sec^{-1}	$[H^+]$, F	10^5k_{obsd}, sec^{-1}
0.100	1.50	0.000127	12.0	0.100[a]	21.9	0.100	91.7	0.110	10.4	0.0500	3.48
0.300	2.58	0.00180	5.07	0.100[a]	21.8	0.200	107	0.50	12.7	0.200	4.46
0.510	3.38	0.0049	4.60	0.200	26.8	0.300	120	1.01	15.5	0.500	6.27
0.71	4.50	0.0095	4.49	0.300	31.2	0.510	139	1.53	18.5	0.70	7.38
0.71	4.44	0.0200	4.61	0.510	37.9	0.71	169	1.91	21.4	0.95	8.96
1.02	5.72	0.100	5.84	0.71	46.4	1.32	240	2.00[a]	21.8		
1.32	6.83	0.300	8.99	0.71	45.4	1.63	287	2.00[a]	21.9		
1.63	8.42	0.510	11.1	1.02	56.6	1.99	318	2.11	23.1		
1.99	9.94	0.71	14.5	1.32	67.6			2.56	27.0		
		0.71	13.5	1.63	79.0			2.94	31.0		
		1.02	17.5	1.99	90.6			3.46	37.8		
		1.32	22.2								
		1.53	24.6								
		1.73	27.8								
		1.99	29.6								

[a] Same datum point entered at two different positions in the table.

(ϵ_{373} 4815 F^{-1} cm^{-1}) after oxidation with basic peroxide.[6] The concentration of 2-mercaptoethylammonium ion in spent reaction mixtures was quantitatively determined by an adaptation of Grassetti and Murray's spectrophotometric thiol analysis.[7] Appropriate blanks containing hexaaquochromium(III) and perchloric acid were employed to demonstrate that, under the conditions of our experiments, these species did not interfere with the thiol analysis.

Kinetic Measurements. The aquation of $[(H_2O)_5CrSCH_2CH_2NH_3]^{3+}$ was followed spectrophotometrically, usually at 274 nm. Reactions were also monitored at 578 and 434 nm, the observed rate constant being independent of the wavelength employed. The ionic strength of reactant solutions was maintained with lithium perchlorate, most experiments having $\mu = 2.00 \pm 0.02\ F$ (see Table I for ranges of ionic strengths and acidities investigated). The presence of oxygen in the reaction solutions was shown to have no effect on the rate of aquation of $[(H_2O)_5CrSCH_2CH_2NH_3]^{3+}$ under any of the conditions studied in this work (in contrast to the catalytic effect of molecular oxygen on the rate of aquation of $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$ [1]). Therefore, most of the experiments reported herein were conducted in the presence of air. Kinetic experiments with a high initial concentration of $[(H_2O)_5CrSCH_2CH_2NH_3]^{3+}$ (monitored in the visible region) were initiated by placing a completely prepared spectrophotometric cell in a constant temperature bath for several minutes; after the cell reached the desired temperature, it was transferred to the thermostated spectrophotometer cell compartment. Kinetic experiments with a low initial concentration of $[(H_2O)_5CrSCH_2CH_2NH_3]^{3+}$ (monitored at 274 nm) were initiated by injecting a small volume (*ca.* 0.025 ml) of concentrated chromium stock solution into a previously thermostated cell containing $HClO_4$ and $LiClO_4$. This more rapid initiation procedure was particularly necessary for studies conducted at higher temperatures.

For most experiments an infinite time measurement (OD_∞) could be determined directly and plots of log ($OD_t - OD_\infty$) *vs.* time gave straight lines for more than 95% of the reaction. Experiments at low temperature and low concentrations of acid proceeded too slowly to conveniently obtain an OD_∞ reading. Therefore, the previously described[2] LASL nonlinear least-squares program was employed to determine the values of k_{obsd}, OD_0, and OD_∞ which best fit the OD_t–t data within the first-order rate expression

$$OD_t = OD_\infty - (OD_\infty - OD_0)e^{-k_{obsd}t} \tag{3}$$

To maintain internal consistency, all kinetic data were treated by this nonlinear technique; where direct comparison was possible, the optimized values of OD_0 and OD_∞ agreed with the observed values to well within experimental error and values of k_{obsd} obtained from the two methods of calculation always agreed to better than 2%. Within each kinetic experiment, the values of OD_t calculated from eq 3 and the optimized values of OD_0, OD_∞, and k_{obsd} always agreed with the observed values of OD_t to a standard deviation of less than 0.0025 optical density unit and on the average to a standard deviation of less than 0.0015 optical density unit.

pK_a Determinations. The 4-mercapto(*N,N,N*-trimethylanilinium) cation was generated *in situ* by the addition of excess 2-mercaptoethanol to a solution of the 4,4′-dithiobis(*N,N,N*-trimethylanilinium) cation. Potentiometric titration with 0.100 *F* NaOH in a 2 *F* LiCl medium [the use of perchlorate was precluded by the insolubility of 4-mercapto(*N,N,N*-trimethylanilinium) perchlorate] led directly to the end point and the desired pK_a. Varying the concentration of 2-mercaptoethanol had no significant effect on the measured pK_a. The pK_a of the 2-mercaptoethylammonium ion was determined by titrating a weighed amount of thiol in the same medium as above. However, in this case the end point was not sharp, and the pK_a of the sulfhydryl group[8] was taken to be the pH at one-half the theoretical end point. Measurements were made at 25°.

Results and Discussion

Synthetic Routes to Thiolatoaquochromium(III) Complexes. The title compound was synthesized by reaction 4 which proceeds *via* electron transfer through sulfur and subsequent transfer of the bridging ligand from cobalt to chromium.

$$Cr_{aq}^{2+} + 5H_3O^+ + (en)_2Co(SCH_2CH_2NH_2)^{2+} \rightarrow (H_2O)_5CrSCH_2CH_2NH_3^{3+} + Co_{aq}^{2+} + 2enH_2^{2+} \tag{4}$$

This method was employed, rather than the simpler reduction of organic disulfide by $[Cr_{aq}]^{2+}$ which was successfully used to prepare[1] $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$, because $[Cr_{aq}]^{2+}$ does not reduce the disulfide of 2-mercaptoethylamine (cystamine) in aqueous perchloric acid. Likewise, $[Cr_{aq}]^{2+}$ does not reduce diethyl disulfide or dimethyl disulfide in water-alcohol solutions of $HClO_4$. The inability of simple alkyl disulfides to oxidize aqueous chromium(II) would seem to be thermodynamic in origin since our polarographic measurements show that the half-wave potential of 2-mercaptoethylamine is 0.5 V greater than that of 4-thioaniline. However, this barrier may be surmounted by appropriate modification of the disulfide. For instance, the half-wave potential of $HSCH_2N(CH_3)_3^+$ is only 0.1 V greater than that of 4-thioaniline and $[Cr_{aq}]^{2+}$ does reduce the corresponding disulfide (albeit very slowly) to yield the alkylthiolatochromium(III) complex directly.

$$10H_2O + 2Cr_{aq}^{2+} + [(CH_3)_3NCH_2S-]_2^{2+} \rightarrow 2(H_2O)_5CrSCH_2N(CH_3)_3^{3+} \tag{5}$$

In addition, the presence of a potential chelating function in the alkyl disulfide will also favor its reduction by chromium(II); both cystine and dithiodiglycolic acid are reduced by $[Cr_{aq}]^{2+}$ to yield the O,S-chelated chromium(III) species.

---

(6) G. W. Haupt, *J. Res. Nat. Bur. Stand.*, **48**, 2331 (1952).

(7) (a) D. R. Grassetti and J. F. Murray, Jr., *Arch. Biochem. Biophys.*, **119**, 41 (1967); (b) D. K. Lavallee, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, **12**, 1440 (1973).

(8) R. E. Benesch and R. Benesch, *J. Amer. Chem. Soc.*, **77**, 5877 (1955).

$$2Cr_{aq}^{2+} + [HOOCCH_2S\text{-}]_2 + 10H_2O \rightarrow 2(H_2O)_4Cr(SCH_2COO)^+ + 2H_3O^+ \quad (6)$$

Characterization of the Pentaaquo(2-mercaptoethylammonium-*S*)chromium(III) Ion. The green $[(H_2O)_5CrSCH_2CH_2NH_3]^{3+}$ ion was identified by (1) the chemistry and high yield of its preparation, (2) its ion-exchange behavior which is consistent with a total formal charge of 3+, (3) the quantitative recovery of its aquation products according to eq 2 (see below), and (4) its ultraviolet spectrum which exhibits an intense peak (274 nm, ϵ 7.00 × 10^3 F^{-1} cm^{-1}, 0.10 *F* $HClO_4$) characteristic of metal-sulfur complexes.[1,5,9-11] This peak is assumed to be a ligand-to-metal charge-transfer band since it disappears upon aquation of the complex. The visible spectrum shows maxima at 438 and 578 nm (ϵ 46 and 26 F^{-1} cm^{-1}, respectively, 10^{-3} *F* $HClO_4$) which are assigned to the derived ${}^4A_{2g} \rightarrow {}^4T_{1g}$ and ${}^4A_{2g} \rightarrow {}^4T_{2g}$ d-d transitions, respectively. The asymmetry of this latter band is much less obvious for this alkylthiolato ligand than it is for the arylthiolato ligand previously reported.[1] As with the halide complexes, the two characterized $[(H_2O)_5CrSR]^{3+}$ complexes show a trend in d-d transitions toward higher wavelength and higher ϵ as ligand polarizability increases.

Aquation of the Pentaaquo(2-mercaptoethylammonium-*S*)chromium(III) Ion. The aquation of $[(H_2O)_5CrSCH_2CH_2NH_3]^{3+}$ was shown to proceed according to the stoichiometry of eq 2 by the recovery of hexaaquochromium(III) and thiol from product mixtures in 99 and 96% yield, respectively. The reaction is first order in complex (see Experimental Section), the observed first-order rate constant (k_{obsd}) being independent of initial concentration of $[(H_2O)_5CrSCH_2CH_2NH_3]^{3+}$ over the range 5×10^{-3}-3×10^{-6} *F*. Table I lists k_{obsd} as a function of acid concentration, temperature, and ionic strength. From both the data at $(H^+) = 0.100$ *F*, varying μ, and the acid dependency at $\mu = 1.00$ and 2.00 *F*, it is clear that the rate of aquation is not very sensitive to the ionic strength of the medium. At $\mu = 2.00$ *F*, 25°, the variation of k_{obsd} with (H^+) may be expressed by

$$k_{obsd} = k_{-1}/(H^+) + k_0 + k_1(H^+) \quad (7)$$

where $k_{-1} = (9.5 \pm 0.7) \times 10^{-9}$ *F* sec^{-1}, $k_0 = (4.5 \pm 0.2) \times 10^{-5}$ sec^{-1}, and $k_1 = (1.31 \pm 0.02) \times 10^{-4}$ F^{-1} sec^{-1} (calculated using the LASL nonlinear least-squares program[2] and the appropriate 15 data points from Table I, errors are standard deviations, average deviation between k_{obsd} and value of k_{obsd} calculated from these optimized parameters and eq 7 is 2.6%). The k_{-1} path seems to be present in aquations of most $[(H_2O)_5CrX]^{n+}$ species, whether X is a strong or weak acid ligand,[12-15] and its observation appears to be dependent upon the range of acid concentrations investigated. In this system we cannot be sure that the k_{-1} path leads to $[(H_2O)_6Cr]^{3+}$ as the sole chromium(III)-containing product. While this is the sole product at acidities as low as 0.01 *F*, at lower acidities aquation could yield products such as the chelated $[(H_2O)_4Cr(SCH_2CH_2NH_2)]^{2+}$ ion, its aquation product *via* Cr-S bond fission, $[(H_2O)_5CrNH_2CH_2CH_2SH]^{3+}$, and polymeric chromium(III) species. The data in Table I show k_{obsd} to increase linearly with (H^+) in the range $(H^+) = 0.100$-1.99 *F*; *i.e.*, k_{-1} contributes negligibly to k_{obsd} at acid concentrations greater than 0.01 *F*. Thus under these conditions the two-term rate law 1 is effective and all 40 appropriate rate constants of Table I [$\mu = 2.00$ *F*, $(H^+) > 0.01$ *F*] were treated simultaneously for all hydrogen ion concentrations and temperatures according to the expression

$$k_{obsd} = \frac{kT}{h}\Sigma_i(H^+)^i e^{\Delta S_i^*/R} e^{-\Delta H_i^*/RT} \quad (8)$$

with $i = 0$ and +1. Each k_{obsd} was weighted by the square of the reciprocal of its standard deviation and the LASL least-squares program[2] was used to calculate the activation parameters which best fit these data. These optimized parameters are $\Delta H_0^* = 27.6 \pm 0.4$ and $\Delta H_1^* = 20.6 \pm 0.3$ kcal/mol, $\Delta S_0^* = 14.0 \pm 1.2$ and $\Delta S_1^* = -7.1 \pm 0.9$ eu (errors are standard deviations, k_{obsd} calculated from these parameters agree with the experimentally determined values with an average deviation of 3.0%).

The two-term rate law 1a

$$-d(\ln\,[(H_2O)_5CrX]^{n+})/dt = k_0 + k_1(H^+) \quad (1a)$$

has been observed for the aquation of $[(H_2O)_5CrX]^{n+}$ ions whenever X is a basic ligand such as fluoride,[12] azide,[13] acetate,[3] cyanide,[14] sulfate,[15] and, of course, the S-bonded thioanilinium ligand.[1] This is generally interpreted as (and in several cases has been shown to be[3,16,17]) the result of a rapid protonation equilibrium preceding rate-determining steps.

$$CrX^{n+} + H^+ \overset{1/K_{a1}}{=} CrXH^{(n+1)+} \quad (9)$$

$$CrX^{n+} \overset{k}{\rightarrow} \text{products} \quad (10)$$

$$CrXH^{(n+1)+} \xrightarrow{k_H} \text{products} \quad (11)$$

This mechanism leads to the rate law

$$\frac{-d\ln(Cr_T)}{dt} = k_{obsd} = \frac{k + k_H(H^+)/K_{a1}}{1 + (H^+)/K_{a1}} \quad (12)$$

where (Cr_T) represents the total concentration of starting material in both protonated and unprotonated forms. When $(H^+)/K_{a1} \ll 1$, this reduces to the observed rate law

$$k_{obsd} = k + k_H(H^+)/K_{a1} \quad (12a)$$

where $k_0 = k$ and $k_1 = k_H/K_{a1}$. The possibility that equilibrium 9 involves protonation at nitrogen is rendered unlikely by the fact that a reasonable estimate for the acid dissociation constant of the $-CH_2NH_3^+$ group of $[(H_2O)_5CrSCH_2CH_2NH_3]^{3+}$ is that of the $-CH_2NH_3^+$ group of $[(NH_3)_5CoOOCCH_2NH_3]^{3+}$, *i.e.*, about 10^{-8}.[18] Thus, the nitrogen functionality of the starting material is completely protonated at all acid concentrations investigated in this work.

Origin of the k_0 Pathway. The nature of the transition state which leads to the k_0 pathway of equation 1a has been the subject of considerable discussion and speculation. Swaddle and King[12,13] noted two possible formulations for this transition state: the first, which we shall refer to as "normal," involves separation of the leaving group, X, from $[(H_2O)_5Cr]^{3+}$; the second, which we shall refer to as "tautomeric," involves separation of HX from $[(H_2O)_4Cr(OH)]^{2+}$. The evidence presented in support of the tautomeric mechanism has largely been negative and indirect in character:

---

[9] R. H. Lane and L. E. Bennett, *Chem. Commun.*, 491 (1971).

[10] M. Ardon and H. Taube, *J. Amer. Chem. Soc.*, 89, 3661 (1967).

[11] C. J. Weschler and E. Deutsch, *Inorg. Chem.*, in press.

[12] T. W. Swaddle and E. L. King, *Inorg. Chem.*, 4, 532 (1965).

[13] T. W. Swaddle and E. L. King, *Inorg. Chem.*, 3, 234 (1964).

[14] J. P. Birk and J. H. Espenson, *Inorg. Chem.*, 7, 991 (1968).

[15] J. Finholt and S. N. Deming, *Inorg. Chem.*, 6, 1533 (1967).

[16] J. C. Templeton and E. L. King, *J. Amer. Chem. Soc.*, 93, 7160 (1971).

[17] D. K. Wakefield and W. B. Schaap, *Inorg. Chem.*, 8, 512 (1969).

[18] R. Holwerda, E. Deutsch, and H. Taube, *Inorg. Chem.*, 11, 1965 (1972).

(1) Swaddle and King,[12,13] and Swaddle,[19] observed that $\Delta S_0{}^*$ increases linearly with $\overline{S}^{\circ}$ (standard partial molal entropy of X, corrected for rotation) when X is Cl^-, Br^-, I^-, $NO_3{}^-$, or NCS^-. When X is $N_3{}^-$ or F^-, this correlation breaks down implying that a different k_0 mechanism is operative. Presumably the strong acid ligands aquate *via* the normal k_0 path, while the weak acid ligands $N_3{}^-$ and F^- aquate by the tautomeric k_0 path. (2) The ratio k_0/k_{-1} for $[(H_2O)_5CrN_3]^{2+}$ is much higher than that for other $[(H_2O)_5CrX]^{n+}$ complexes where X is a strong acid ligand.[20] Again this implies that the weak acid ligand aquates *via* a different mechanism. (3) Espenson[21] correlated the rate constants for several ligation reactions of $[(H_2O)_6Cr]^{3+}$. He found that the coefficients of the rate term $[Cr^{3+}][HX]/[H^+]$, where X was F^- or $N_3{}^-$, were more consistent with the anation rates of strong acid ligands if they were interpreted as reactions between HX and $[(H_2O)_5Cr(OH)]^{2+}$ rather than between X^- and $[(H_2O)_6Cr]^{3+}$. (4) Wakefield and Schapp[17] found that k_0 for the aquation of $[(H_2O)_5CrCN]^{2+}$ was not strongly dependent on the nature of the ionic medium and commented that this is consistent with the leaving group being a neutral HX molecule.

If, when X is a ligand derived from a weak acid, both k_0 and k_1 proceed *via* protonation of the ligand, one would expect some sort of correlation between these rate parameters and the basicity of free X. Attempts at this type of correlation have been made. (1) Espenson and Binau[22] tried unsuccessfully to correlate k_1/k_0 ratios with the base strength of the free ligand X. (2) Brown and Cooper[23] have shown that k_1 decreases with decreasing pK_a of the common mononegative basic ligands and have compiled an appropriate table. (3) Monacelli[24] correlated k_0 for $[(H_2O)_5CrX]^{2+}$ aquations, X = strong acid anions I^-, Br^-, Cl^-, and NCS^- and weak acid anions F^- and $N_3{}^-$, with the pK_a of the free ligand (using those estimated pK_a's for the strong acid ligands which have correlated organic reactions[25]). He noted a linear relationship for all ligands except azide and suggested that the azido complex aquates *via* a different mechanism than do the others.

An instructive correlation may be made by formally separating the tautomeric k_0 path into the following component steps.

$$(H_2O)_5CrX^{n+} \overset{K_w}{=} (H_2O)_4(OH)CrX^{(n-1)+} + H^+ \tag{10a}$$

$$H^+ + (H_2O)_4(OH)CrX^{(n-1)+} \overset{1/K_{a0}}{=} (H_2O)_4(OH)CrXH^{n+} \tag{10b}$$

$$(H_2O)_4(OH)CrXH^{n+} \xrightarrow{k_T} \text{products} \tag{10c}$$

It should be expressly noted that this is just a formalism designed to illuminate the forces driving proton transfer from coordinated water to X; the proton may never be released to solution. This internal hydrogen shift may occur rapidly before rate-limiting dissociation of HX, or the proton may be transferred to X as the Cr-X bond is stretched. Equations 10a-c lead to the expression

$$k_0 = k_T(K_w)/K_{a0} \tag{10d}$$

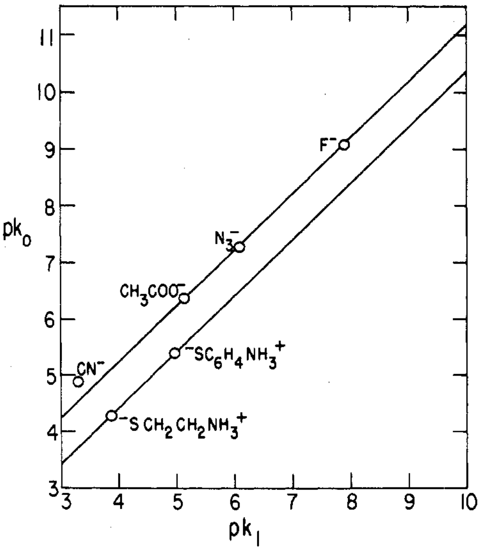


Figure 1. pk_0 *vs.* pk_1 for aquation of $[(H_2O)_5CrX]^{n+}$ complexes which show both k_0 and k_1 paths. Lines of slope = 1.0 are indicated. All pk_i values are at 25° and μ = 1.00 *F* ($LiClO_4$) except for thiolato ligands at μ = 2.00 *F* ($LiClO_4$). (This offset is not a result of the difference in ionic strength at which kinetics were studied. The position of the $[(H_2O)_5CrSCH_2CH_2NH_3]^{3+}$ point is not appreciably affected by substituting k_0 and k_1 values determined at μ = 1.00 *F*.) References for pk_i of $SO_4{}^{2-}$, CN^-, $N_3{}^-$, F^-, CH_3COO^-, $^-SC_6H_4NH_3{}^+$, and $^-SCH_2CH_2NH_3{}^+$ are 15, 14, 13, 12, 3, 1, and this work, respectively.

Since K_{a0} and K_{a1} represent the acid dissociation constants of HX when bound to $[(H_2O)_4(OH)Cr]^{2+}$ and $[(H_2O)_5Cr]^{3+}$, respectively, it is not unreasonable to expect them to be closely related. If one makes the assumption that K_{a0} is proportional to K_{a1}, then eq 12a and 10d lead to the relationship

$$\log (k_1) = \log (k_0) + \log (Ak_H/K_wk_T) \tag{13}$$

where $A = K_{a0}/K_{a1}$. This predicts that, if the ratio Ak_H/K_wk_T remains constant for all complexes treated, a plot of pk_0 *vs.* pk_1 will be linear with unit slope. Figure 1 shows this plot, in which two distinct lines of unit slope are defined by the zwitterionic thiolato ligands and the mononegative ligands (the small deviation of the point for CN^- is attributed to the relatively large uncertainties in the activation parameters used to calculate k_0 and k_1 for this complex[26]). The offset between these two lines is attributed to the dependency of the intercept term in eq 13 on the net charge of the complex. While all four of the parameters of the intercept term are expected to be somewhat charge-dependent, A and K_w are probably the most sensitive. The effect of net complex charge could also explain why the point for sulfate does not correlate with the other complexes, but it is also possible that the sulfato complex aquates *via* the normal k_0 mechanism[15] (see below: $HSO_4{}^-$ is the strongest acid considered here) and there is always the ambiguity as to whether aquation involves Cr-O or S-O bond fission.

Thus, Figure 1 provides strong evidence that, in the aquation of $[(H_2O)_5CrX]^{n+}$ complexes of ligands derived from weak acids, k_0 and k_1 are similarly dependent on the ability of the coordinated ligand to be protonated. Since it is well established that the k_1 pathway involves a protonated intermediate, this provides the first positive evidence for the tautomeric k_0 reaction pathway. It is interesting to note that while the constancy of k_0/k_1 for weak acid ligands is diag-

---

(19) T. W. Swaddle, *J. Amer. Chem. Soc.*, 89, 4338 (1967).

(20) L. R. Carey, W. E. Jones, and T. W. Swaddle, *Inorg. Chem.*, 10, 1566 (1971).

(21) J. H. Espenson, *Inorg. Chem.*, 8, 1554 (1969).

(22) J. H. Espenson and D. E. Binau, *Inorg. Chem.*, 5, 1365 (1966).

(23) L. S. Brown and J. N. Cooper, *Inorg. Chem.*, 11, 1154 (1972).

(24) F. Monacelli, *Ric. Sci.*, 37, 777 (1967).

(25) J. O. Edwards, *J. Amer. Chem. Soc.*, 76, 1540 (1954).

(26) These parameters were used because they were obtained in $LiClO_4$ medium (ref 14) as were the other data. More precise values obtained in $NaClO_4$ medium (ref 17) give values of k_0 and k_1 which lie much closer to the indicated line of Figure 1.

nostic of the tautomeric k_0 path, the constancy of k_0/k_{-1} for strong acid ligands is diagnostic of the normal k_0 path[19] (both $[(H_2O)_5CrN_3]^{2+}$ and $[(H_2O)_5CrSCH_2CH_2NH_3]^{3+}$ have a k_0/k_{-1} ratio about 10^3 times greater than that observed for strong acid ligands). This duality of k_0 mechanisms is seen more clearly in Figure 2 where Monacelli's pk_0 *vs.* pK_a plot is extended from strong to weak acid ligands. It is clear that a definite change in slope, and therefore presumably mechanism, occurs around a pK_a value of 1-2. For acids stronger than this, k_0 seems to be governed by solvation of the leaving ligand as expected for the normal k_0 mechanism (and the k_{-1} pathway); for acids weaker than this, k_0 seems to be governed by the ability of the coordinated ligand to be protonated as expected for the tautomeric k_0 mechanism (and the k_1 pathway). The linearity in the strong acid region is largely due to a fortuitous choice of pK_a values by Monacelli[24] who used strong acid pK_a's that were estimated in correlating organic nucleophilic displacement reactions.[25] The lack of linearity in the weak acid region is not surprising since, from eq 10d, linearity would demand that $K_{a0}/K_a = B$ with B being the same for all complexes. This is especially unlikely since there is an ambiguity as to the protonation site for many of the ligands considered (*i.e.*, the ligand atom being protonated in the complex is not necessarily the same atom which is protonated in the free ligand). The same reason mitigates against a linear pk_1 *vs.* pK_a plot (from eq 12a, K_{a1} would have to be proportional to K_a) and, as predicted by Figure 1, such a plot closely resembles the weak acid portion of Figure 2. Nonlinearity of the pk_0 and pk_1 *vs.* pK_a plots is also engendered by the inconstancy of k_H, k_T, and possibly K_w as ligands are varied; however, the linearity of Figure 1 implies that the ratio of k_H to k_T is constant for ligands of the same charge type.

For two pentaaquochromium(III) complexes of closely related ligands, the relative ease of protonation of the coordinated ligands should not be dependent upon whether they are coordinated to $[(H_2O)_5Cr]^{3+}$ or to $[(H_2O)_4(OH)Cr]^{2+}$. Therefore, if the relative ease of protonation of the coordinated ligand is important in determining both k_0 and k_1, one could reasonably expect to observe a simple relationship between the respective activation parameters for two complexes so similar that all factors other than ligand basicity may be assumed to be identical. There are now available detailed kinetic data for two such closely related complexes, $[(H_2O)_5CrSR]^{3+}$ with R being the aryl group $-C_6H_4NH_3^+$ and the alkyl group $-CH_2CH_2NH_3^+$, and indeed the differences in activation parameters (aryl minus alkyl) for the k_0 terms are equal, within experimental error, to the respective differences for the k_1 terms [$\Delta(\Delta H_0^*) = 2.2 \pm 0.8$ and $\Delta(\Delta H_1^*) = 3.1 \pm 0.8$ kcal/mol; $\Delta(\Delta S_0^*) = 2.7 \pm 2.3$ and $\Delta(\Delta S_1^*) = 5.0 \pm 2.2$ eu]. Assuming that the activation parameters governing k_H and k_T (and the $\Delta H°$, $\Delta S°$ governing K_w) for the alkyl complex are identical with the respective parameters for the aryl complex, these differences are identified as $\Delta(\Delta H_{K_a}°)$ and $\Delta(\Delta S_{K_a}°)$, *i.e.*, the extra enthalpy and entropy required to protonate coordinated $-SC_6H_4NH_3$ relative to the more basic coordinated $-SCH_2CH_2NH_3$.

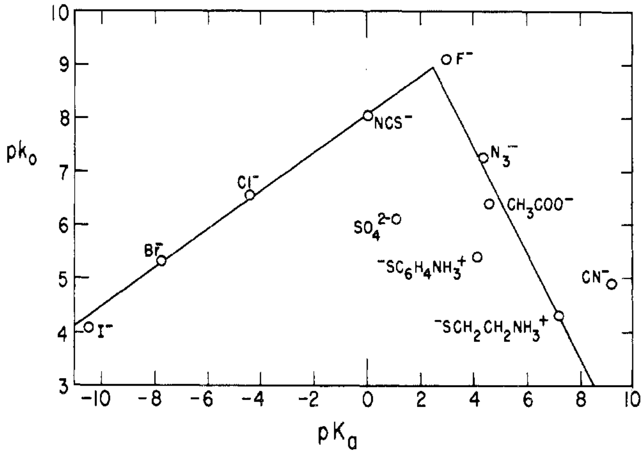
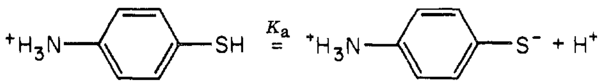


Figure 2. pk_0 for aquation of $[(H_2O)_5CrX]^{n+}$ *vs.* pK_a of HX for those ligands correlated by Monacelli[24] and herein. pK_a values of strong acids were obtained by Monacelli from ref 25. pK_a values for weak acids are at 25° and the same μ as corresponding pk_0 (see Figure 1 caption), except for CN^- reported at μ extrapolated to zero. Weak acid pK_a values, except for thiolato ligands, were taken from L. G. Sillen and A. E. Martell, "Stability Constants of Metal Ion Complexes," *Chem. Soc., Spec. Publ.,* **No. 17**, (1964); pK_a's of $HSCH_2CH_2NH_3^+$ (-SH proton) and $HSC_6H_4N(CH_3)_3^+$ were measured (this work) in 2.0 *F* LiCl as 7.2 ± 0.1 and 4.1 ± 0.1, respectively. Arbitrary line of slope = −1.0 drawn in weak acid region. The K_a of 4-mercapto(*N,N,N*-trimethylanilinium) cation was used as the best approximation to the theoretical K_a governing the equilibrium



Registry No. $[Co(en)_2(SCH_2CH_2NH_2)](ClO_4)_2$, 40330-50-5; $[Co(en)_2(SCH_2CH_2NH_2)]I_2$, 40192-34-5; $[Cr(H_2O)_5(SCH_2CH_2NH_2)]^{2+}$, 40192-35-6.

Acknowledgments. We acknowledge the general support of the Materials Research Laboratory by the National Science Foundation. Funds for this work were also provided through an IBM General Grant; L. E. A. was the recipient of a La Verne Noyes Foundation Scholarship. We are also indebted to Mr. Scot Wherland for the preparation of salts and derivatives of the trimethylmercaptomethylammonium cation.