plex was converted to the corresponding diaquobis chromium(III) complex and free ligand in the presence of catalytic quantities of tris chromium(II) produced by reduction of the tris chromium(III) at a mercury surface at −0.60 V. The rate of conversion is faster for the bipyridine than the phenanthroline complex and both are temperature dependent. Although the tris chromium(II) complex is in equilibrium with the diaquobis chromium(II) complex, the tris complex is favored. The tris(1,10-phenanthroline) complexes of Cr(II), Cr(I), and Cr(0) can be prepared by successive one-electron reduction of the tris Cr(III) complex. The black, water-insoluble tris Cr(0) complex can be oxidized to the tris Cr(III) with oxygen in a system void of quantities of reduced materials.

Acknowledgment.—The authors would like to thank Hilda Jung for preparation of the figures.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF CHICAGO,
CHICAGO, ILLINOIS 60637

Preparation and Aquation Kinetics of the Pentaaquo(4-thioanilinium-*S*)chromium(III) Ion. Catalysis of Chromium–Sulfur Bond Breaking by Oxygen and Other Oxidants

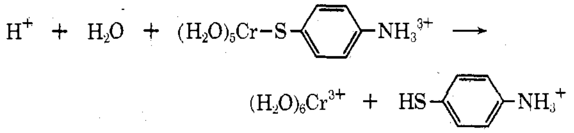
BY LEON E. ASHER AND EDWARD DEUTSCH*

Received May 16, 1972

The pentaaquo(4-thioanilinium-*S*)chromium(III) ion has been prepared *via* chromium(II) reduction of *p*-aminophenyl disulfide in aqueous acid and subsequent ion-exchange separation from by-products. In aqueous perchloric acid, under anaerobic conditions, this complex aquates according to the rate law $-d[\ln (CrSR^{3+})]/dt = k_0 + k_1(H^+)$. At $\mu = 2.00$ *F* ($LiClO_4$), the specific rate constants extrapolated to 25° and their corresponding activation parameters have the values $k_0 = 4.0 \times 10^{-6}$ sec^{-1}, $\Delta H_0^* = 29.8 \pm 0.7$ kcal/mol, and $\Delta S_0^* = 16.7 \pm 2.0$ eu and $k_1 = 11.0 \times 10^{-6}$ M^{-1} sec^{-1}, $\Delta H_1^* = 23.6 \pm 0.7$ kcal/mol, and $\Delta S_1^* = -2.1 \pm 1.9$ eu. In the presence of oxygen, $CrSR^{3+}$ aquates *via* an autocatalytic mechanism with *p*-aminothiophenol being the catalytic agent. Hydrogen peroxide and iron(III) also catalyze the aquation of $CrSR^{3+}$ according to the rate law $-d[\ln (CrSR^{3+})]/dt = k$(oxidant). It is suggested that the catalyzed aquations proceed *via* oxidation of coordinated thiolate to a relatively labile coordinated free radical. Hydrogen peroxide, iron(III), and $\cdot SR^+$, but not molecular oxygen, are effective oxidants.

Introduction

The chemistry of $(H_2O)_5CrX^{n+}$ complexes has received considerable attention in recent years, not only because these ions constitute one of the simplest systems in which to study the kinetics of chromium–ligand bond breaking, but also because they are often the products of chromium(II) inner-sphere reductions in aqueous solution.[1] Complexes in which X is a halide or pseudohalide, or in which X is coordinated through a nitrogen or oxygen atom, have been extensively investigated,[2] but except for one brief communication[3] there have been no reports on complexes in which X is coordinated through a thiolato sulfur atom. Detailed studies of well defined $(H_2O)_5CrSR^{n+}$ complexes should be very useful in delineating the role of metal–thiol interactions in complex biological systems such as those involving nonheme iron–sulfur proteins,[4] in defining more clearly the complicated mechanisms of metal ion catalyzed autoxidation of thiols,[5] and in extending our general knowledge of ligands which coordinate through second row elements. Progress in this area has until now been hindered by the lack of a convenient procedure for the synthesis of $(H_2O)_5CrSR^{n+}$ complexes. However, our interest in the reduction of organic disulfides by chromium(II) has led to simple procedures for the preparation of certain thiolatopentaaquochromium(III) ions, and in turn to an investigation of the chemistry of these ions. In this paper we report on the preparation and aquation in aqueous acidic media of the pentaaquo(4-thioanilinium-*S*)chromium(III) ion and its trimethylammonium analog, these ligand systems having been chosen because of their water solubility. The catalysis of this aquation by oxygen, hydrogen peroxide, and other oxidants is also described; the possible significance of these results, in terms of the mechanism of metal ion catalyzed autoxidation of thiols, is indicated. Under nitrogen, the net equation for the aquation reaction is



(1)

Experimental Section

Equipment.—Pmr spectra were recorded on a Varian A-60 at 37° and shifts are reported relative to tetramethylsilane. Visible and ultraviolet spectra were recorded on a Cary 14 spectrophotometer at room temperature. Millivolt and pH readings were obtained with a Beckman Research pH meter. Kinetic runs were followed on a Cary 16K spectrophotometer equipped with a thermostatted cell compartment that maintained the temperature of reacting solutions to better than ±0.2°. Computer calculations were done on an IBM System 360 located at The University of Chicago Computation Center. The standard

---

(1) H. Taube and E. S. Gould, *Accounts Chem. Res.*, **2**, 321 (1969).

(2) For a general review of literature through 1965, see J. E. Earley and R. D. Cannon, *Transition Metal Chem.*, **1**, 33 (1965). More recent references are quoted in A. Bakac and M. Orhanovic, *Inorg. Chem.*, **10**, 2443 (1971).

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

(4) R. Malkin and J. C. Rabinowitz, *Annu. Rev. Biochem.*, **36**, 113 (1967).

(5) C. J. Swan and D. L. Trimm, *Advan. Chem. Ser.*, **76**, 182 (1968); J. D. Hopton, C. J. Swan, and D. L. Trimm, *ibid.*, **75**, 216 (1968), and references therein.

Los Alamos nonlinear least-squares program was adapted to this system and used for all data analysis.[6]

Materials.—All common laboratory chemicals were of reagent grade. Water was distilled two times in Pyrex equipment. G. Frederick Smith doubly distilled perchloric acid was used for kinetics. Dowex 50W-X2 ion-exchange resin, 200–400 mesh, was kindly donated by Dow Chemical Co. and was cleaned by a previously outlined procedure.[7] Lithium perchlorate, hexaaquochromium(III) perchlorate, and solutions of chromium(II) perchlorate were prepared as previously described.[7] Technical grade *p*-aminophenyl disulfide was obtained from Aldrich Chemical Co. and purified by repeated extraction of the free base into ether and back-extraction of the protonated form into aqueous acid, subsequent treatment with decolorizing charcoal, and a final crystallization from hot aqueous ethanol, uncor mp 75–77° (lit. mp 74–76°).[8] Reagent grade *p*-aminothiophenol was obtained from Aldrich Chemical Co. and purified by vacuum distillation. *p*-Dimethylaminophenyl disulfide was prepared *via* the reaction of sulfur monochloride with *N*,*N*-dimethylaniline in petroleum ether according to Merz and Weith,[9] uncor mp 116–117° (lit. mp 118°).[8] This was converted to the 4,4′-dithiobis(*N*,*N*,*N*-trimethylanilinium) cation[10] by methylation with either methyl iodide or dimethyl sulfate in refluxing 2-butanone. The resulting water soluble iodide and methylsulfonate salts are easily converted to the slightly soluble perchlorate salt by treatment with perchloric acid and recrystallization from warm water. Pmr spectra and elemental analyses of the purified salts are consistent with the proposed formulation, but do not exclude the possible presence of small amounts of the $[(CH_3)_3NC_6H_4SSC_6H_4NH(CH_3)_2]^{2+}$ cation. However, the evidence does show that this impurity is present at levels of less than 5% in any of the preparations used in this work. The pmr spectrum of the methylsulfonate salt in DMSO-d_6 consists of an *O*-CH_3 singlet at τ 6.55 (3H), an *N*-CH_3 singlet at τ 6.35 (9H), and aromatic peaks at τ 2.27, 2.12, 1.97, and 1.81 (4H). *Anal.* Calcd for $C_{18}H_{26}N_2S_2(ClO_4)_2$: C, 40.53; H, 4.91; N, 5.25; S, 12.02. Found: C, 39.76; H, 5.18; N, 5.18; S, 12.29.

Preparation of Pentaaquo(4-thioanilinium-*S*)chromium(III) Solutions.—Solutions of the pentaaquo(4-thioanilinium-*S*)chromium(III) ion were prepared by reduction of *p*-aminophenyl disulfide with chromium(II) in aqueous perchloric acid and subsequent ion exchange of the reaction mixture. In a typical preparation, 8.5 mmol of disulfide were dissolved in 50 ml of 1 *F* perchloric acid and the resulting solution deoxygenated by bubbling nitrogen through it. Six milliliters of 1.5 *F* chromium(II) perchlorate solution were then added, reduction of the disulfide occurring rapidly. The resulting green solution was diluted to approximately 0.5 *F* ionic strength and added to a Dowex 50 W-X2 ion-exchange column which had previously been rinsed with 0.5 *F* $LiClO_4$. Initial elution with 1 *F* $LiClO_4$ (0.001 *F* in $HClO_4$) separated the green 3+ pentaaquo(4-thioanilinium-*S*)chromium(III) band and the blue 3+ hexaaquochromium(III) band from more highly charged polymeric materials. Subsequent slow elution with 2 *F* $LiClO_4$ (0.001 *F* in $HClO_4$) then brought off the blue band slightly ahead of the green one. Because complete separation of the two 3+ species on a single column is very difficult and because hexaaquochromium(III) slowly grows into stock solutions of the pentaaquo(4-thioanilinium-*S*)chromium(III) ion as the only chromium-containing product of the aquation reactions, most of the preparations used for kinetics contained about 5% of hexaaquochromium(III). One preparation was repeatedly subjected to the above ion-exchange procedure until the effective extinction coefficient (optical density divided by total chromium concentration) at 595 nm remained constant. This was taken to be the extinction coefficient of the pentaaquo(4-thioanilinium-*S*)chromium(III) ion and it was used, with the known extinction coefficient of the hexaaquochromium(III) ion at this wavelength,[7] to calculate the concentration of pentaaquo(4-thioanilinium-*S*)chromium(III) in various preparations, usually about 0.01 *F*. The overall yield of pentaaquo(4-thioanilinium-*S*)chromium(III) in a typical preparation is usually over 75%, in several cases being considerably higher. All ion-exchange separations were carried out in a cold room at 5–7° in order to inhibit aquation, and the final solutions were stored under nitrogen at approximately −10°. Solutions of the pentaaquo(4-thio-*N*,*N*,*N*-trimethylanilinium-*S*)chromium(III) ion were prepared in a similar fashion, except that a salt of the 4,4′-dithiobis(*N*,*N*,*N*-trimethylanilinium) cation was used to oxidize chromium(II). The methylsulfonate salt proved to be best suited for this synthesis, although preparations were also run using the slightly soluble perchlorate salt.

Analyses.—Elemental analyses of solid compounds were performed by PCR Inc. of Gainesville, Fla. The total perchlorate concentration of a solution was determined with a Corning No. 47613 perchlorate sensitive electrode which had been standardized against neutralized perchloric acid and recrystallized potassium perchlorate. The total chromium concentration of solutions was measured spectrophotometrically as chromate (ϵ_{373} 4815) after oxidation with basic hydrogen peroxide.[11] The total sulfur content of a solution was determined gravimetricaly as $BaSO_4$ after wet oxidation with a mixture of nitric and perchloric acids.[12] Application of this analysis to the determination of S/Cr ratios of pentaaquo(4-thioanilinium-*S*)chromium(III) stock solutions uncovered several complicating factors which tended to reduce the theoretical precision of the method and give systematically low S/Cr values. The average of ten determinations of the S/Cr ratio was 0.97 ± 0.03 (99% confidence limit), providing strong evidence for a one-to-one complex. The aquation products *p*-aminothiophenol and *p*-aminophenyl disulfide were qualitatively identified by pmr spectroscopy (chemical shifts of aromatic protons ortho to sulfur differ by 6 cps for these two compounds) and by thin-layer chromatography (Eastman 6060 silica plates with fluorescent indicator; 6:2:1 cyclohexane–benzene–ethanol;[13] R_f = 0.6 and 0.3 for mercaptan and disulfide, respectively). The concentration of *p*-aminothiophenol in spent reaction mixtures was quantitatively determined by an adaptation of Grassetti and Murray's[14] spectrophotometric thiol analysis which utilizes the reduction of 2,2′-dithiodipyridine (obtained from Aldrich Chemical Co.). The absorbance of the resulting 2-thiopyridone was shown to be proportional to the concentration of *p*-aminothiophenol under the conditions of our experiments by the use of appropriate blanks and calibration curves.

Kinetic Measurements.—The aquation of $(H_2O)_5CrSC_6H_4NH_3^{3+}$ and $(H_2O)_5CrSC_6H_4N(CH_3)_3^{3+}$ was followed spectrophotometrically, usually at 595 nm. Reactions were also monitored at 370 and 300 nm, the observed rate constant being independent of the wavelength employed. For experiments performed under nitrogen, unless otherwise noted, the ionic strength of reactant solutions was maintained with lithium perchlorate, most runs having μ = 2.00 ± 0.02 *F*. The dependence of the anaerobic aquation rate on ionic strength was determined over the range μ = 0.14–3.20 *F* (see Table I) establishing that the observed rate constant is relatively insensitive to small variations in ionic strength in the region of μ = 2.00 *F*. Changing the supporting electrolyte from $LiClO_4$ to $NaClO_4$ at (H^+) = 1.0 *F* results in only a small (*ca.* 10%) decrease in the observed anaerobic rate constants. For aquation in the absence of oxygen, a nitrogen stream was deoxygenated and equilibrated with water by passage through scrubbing towers containing an acidic solution of chromium(II) perchlorate. The stream was then bubbled through each serum capped reaction cell for at least 10 min at room temperature. The cells were then placed in a water bath, which was held at the working temperature, for several minutes and then were placed in the thermostatted cell compartment. For aquation in the presence of oxygen, either air or oxygen gas was equilibrated with aqueous acid in a scrubbing tower and then bubbled through the cells. In some runs the cells were then sealed off and no longer exposed to oxygen, while in others oxygen was continuously bubbled through the solution. Experiments designed to check the effect of reaction products were performed by injecting a small volume of a concentrated solution of the appropriate product into a reaction solution which had already been equilibrated with the appropriate gas stream.

For the anaerobic experiments, an infinite time measurement (OD_∞) could conveniently be determined in kinetic runs at 40,

---

[6] R. H. Moore and R. K. Zeigler, Los Alamos Scientific Laboratory Report No. LA-2367, 1959, plus Addenda. We are very grateful to Dr. T. W. Newton (LASL, CMF-2) for providing us with a copy of this program and for assisting us in its utilization.

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

[8] H. Wojahn and I. Lerch, *Arzneim.-Forsch.*, **2**, 455 (1952).

[9] V. Merz and W. Weith, *Ber.*, **19**, 1570 (1886).

[10] G. Schwarzenbach and E. Rudios, *Helv. Chim. Acta*, **22**, 371 (1939).

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

[12] P. O. Bethge, *Anal. Chem.*, **28**, 119 (1956).

[13] K. Papke and R. Pohloridek-Fabini, *J. Chromatogr.*, **36**, D69 (1968).

[14] D. R. Grassetti and J. F. Murray, Jr., *Arch. Biochem. Biophys.*, **119**, 41 (1967).

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE ANAEROBIC AQUATION OF $(H_2O)_5CrSC_6H_4NH_3^{3+}$ AS A FUNCTION OF TEMPERATURE, ACID CONCENTRATION, AND IONIC STRENGTH ($LiClO_4$)

29.8°, μ = 2.00 *F*		39.3°, μ = 2.00 *F*		48.8°, μ = 2.00 *F*		58.4°, μ = 2.00 *F*		39.3°, [H⁺] = 0.10 *F*	
$[H^+]$, *M*	10^5k_{obsd}, sec^{-1}	$[H^+]$, *M*	10^5k_{obsd}, sec^{-1}	$[H^+]$, *M*	10^5k_{obsd}, sec^{-1}	$[H^+]$, *M*	10^5k_{obsd}, sec^{-1}	μ, *M*	10^5k_{obsd}, sec^{-1}
0.13	1.30	0.05	4.59	0.13	19.6	0.05	73.4	0.14	2.57
0.30	1.77	0.05	4.70	0.30	23.8	0.10	74.4	0.16	3.05
0.51	2.16	0.10	4.53	0.51	30.6	0.20	82.2	0.21	2.59
0.51	2.19	0.20	5.19	0.51	28.7	0.20	83.6	0.33	2.87
0.72	2.84	0.20	5.29	0.72	34.8	0.51	99.8	0.35	2.78
0.72	2.81	0.30	6.11	0.72	35.4	0.51	104	0.50	2.91
1.03	3.20	0.30	5.89	1.03	41.9	0.72	118	0.64	2.89
1.23	3.76	0.51	7.52	1.23	47.3	0.72	114	1.14	3.47
		0.51	7.11			0.72	118	1.47	3.72
		0.72	8.72			1.03	137	1.72	4.11
		0.72	8.88			1.23	157	2.00	4.53
		1.03	10.9			1.23	143	2.33	4.73
		1.03	11.2			1.46	169	2.88	5.13
		1.23	11.6			1.46	173	3.23	6.72
		1.33	13.1						
		1.33	13.1						

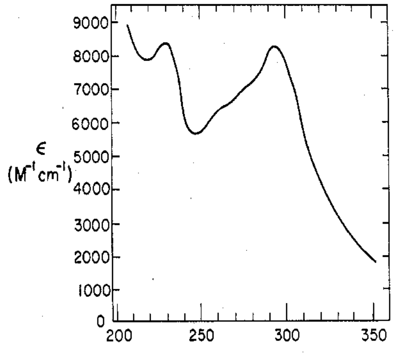


Figure 1.—Ultraviolet spectrum of the $(H_2O)_5CrSC_6H_4NH_3^{3+}$ ion in 0.10 *F* $HClO_4$.

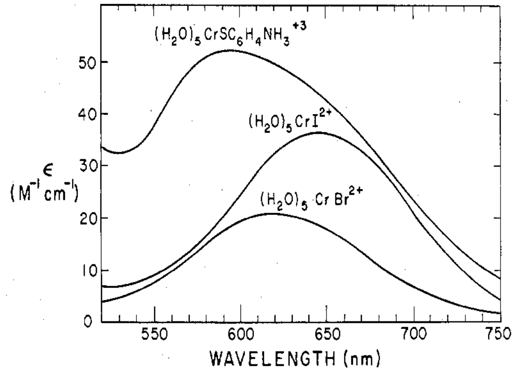


Figure 2.—Portions of the visible spectra of the $(H_2O)_5CrSC_6H_4NH_3^{3+}$, $(H_2O)_5CrI^{2+}$, and $(H_2O)_5CrBr^{2+}$ ions in 0.001, 1.0, and 1.0 *F* $HClO_4$, respectively.

50, and 60°. For these, plots of log $(OD_t - OD_\infty)$ *vs.* time gave straight lines for more than 90% of the reaction, several runs exhibiting first-order behavior for more than 97% of the reaction. The initial concentration of $(H_2O)_5CrSC_6H_4NH_3^{3+}$ was varied over the range 2.0×10^{-4}–1.0×10^{-2} *F*, first-order kinetics being observed over this entire range. Kinetic runs at 30° proceeded too slowly to conveniently obtain an OD_∞ reading. The first-order rate constants for these runs with undetermined OD_∞'s were calculated using Kezdy's time-lag method,[15] a legitimate procedure since first-order kinetics has been established at the higher temperatures. First-order rate constants for those runs in which OD_∞ was determined were also calculated by the time-lag method, as well as from log $(OD_t - OD_\infty)$ plots, and in all cases the two rate constants agreed to within 2%. To maintain internal consistency, all the rate constants reported in Table I were calculated by the time-lag method. The slope of each individual time-lag plot was determined by a linear least-squares calculation[16] which also yielded the standard deviation of the slope (σ_{slope}). The standard deviation of the rate constant (σ_k) was calculated from σ_{slope} *via* the expression[17]

$$\sigma_k = \frac{\sigma_{slope}}{(\text{slope})(\text{time interval})}$$

and σ_k was later used to weight individual kinetic runs for the determination of activation parameters.

Results and Discussion

Characterization of the Pentaaquo(4-thioanilinium-*S*)chromium(III) Ion.—The green $(H_2O)_5CrSC_6H_4NH_3^{3+}$ ion was identified by (1) the chemistry and high yield of its preparation, (2) its S/Cr ratio of 0.97 ± 0.03 which we are confident represents a one-to-one complex, (3) its ion-exchange behavior which is consistent with a total formal charge of 3+, and (4) the products of its aquation under nitrogen which are identified below as hexaaquochromium(III) and the 4-thioanilinium ion. The ultraviolet spectrum of this ion (Figure 1) shows maxima at 295 nm (ϵ 8250 M^{-1} cm^{-1}) and 230 nm (ϵ 8400 M^{-1} cm^{-1}) in 0.1 *F* perchloric acid. The latter peak arises from the ligand itself while the former is assumed to be a ligand-to-metal charge transfer band since it disappears upon aquation of the complex. The 295-nm peak tails so far into the visible that it hides the $^4A_{2g} \rightarrow {}^4T_{1g}$ derived d–d transitions that one would normally expect around 410 nm for a $(H_2O)_5CrX^{n+}$ ion.[18] However, the $^4A_{2g} \rightarrow {}^4T_{2g}$ derived transitions are observed, and in Figure 2 this peak is illustrated along with the corresponding peaks for $(H_2O)_5CrBr^{2+}$ and $(H_2O)_5CrI^{2+}$. The asymmetry of this band is much more obvious for the thiolate ligand than for either of the halides, and following Perumareddi[18] we assign the peak at 595 nm (ϵ 52 M^{-1} cm^{-1}) to $^4B_1(^4A_{2g}) \rightarrow {}^4B_2(^4T_{2g})$ and attribute the asymmetry to $^4B_1(^4A_{2g}) \rightarrow {}^4E_a(^4T_{2g})$ at *ca.* 640 nm. Two other compounds of the pentaaquochromium(III)

---

(15) F. J. Kezdy, J. Jaz, and A. Bruylants, *Bull. Soc. Chim. Belg.*, **67**, 687 (1958).

(16) D. C. Baird, "Experimentation, An Introduction to Measurement Theory and Experiment Design," Prentice-Hall, Englewood Cliffs, N. J., 1962, p 186.

(17) C. H. Bamford and C. F. H. Tipper, "Comprehensive Chemical Kinetics," Vol. 1, Elsevier, New York, N. Y., 1969, p 371.

(18) J. R. Perumareddi, *Coord. Chem. Rev.*, **4**, 73 (1969).

series containing a Cr–S bond have been reported, although neither of them exhibits such clear-cut distortion of this band. The $(H_2O)_5CrSCN^{2+}$ ion[19] has a peak at 620 nm, presumably the ^4E_a transition, indicating that S-bonded thiocyanate is adjacent to bromide (comparable peak at 622 nm) in the spectrochemical series, while thiophenolate is much closer to iodide (peaks at *ca.* 640 and 650 nm, respectively). The $(H_2O)_5CrSH^{2+}$ ion[20] exhibits two bands at 574 and 434 nm which are presumed to be, respectively, the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ derived transitions. On repeating Ardon's preparation, our isolated 2+ band exhibits peaks at 578 and 418 nm (ϵ 29 and 56 M^{-1} cm^{-1}, respectively).

Anaerobic Aquation of the Pentaaquo(4-thioanilinium-*S*)chromium(III) Ion.—When carried out under a nitrogen blanket, the aquation of $(H_2O)_5CrSC_6H_4NH_3^{3+}$ was shown to proceed according to the stoichiometry of eq 1 by the recovery of hexaaquochromium(III) in 97% yield and *p*-aminothiophenol in 88% yield. The first-order rate constants obtained for this process (k_{obsd}) as a function of acid concentration, temperature, and ionic strength, are given in Table I. It is seen that at constant ionic strength and temperature this parameter increases linearly with increasing perchloric acid concentration. Thus the two-term rate law

$$\frac{-\mathrm{d}\ln(\mathrm{CrSR}^{3+})}{\mathrm{d}t} = k_{obsd} = k_0 + k_1(\mathrm{H}^+) \qquad (2)$$

is effective and the 46 rate constants in Table I, obtained at $\mu = 2.00$ *F*, were treated simultaneously for all hydrogen ion concentrations and temperatures according to the expression

$$k_{obsd} = \left(\frac{kT}{h}\right)\sum_i (\mathrm{H}^+)^i e^{\Delta S_i^*/R} e^{-\Delta H_i^*/RT}$$

with $i = 0$ and $+1$. The LASL nonlinear least-squares program previously described[6] was used to calculate the values of the enthalpies and entropies of activation that best fit this data. Each k_{obsd} was weighted by the reciprocal of its standard deviation, obtained from the individual linear time-lag plot. The activation parameters calculated by this procedure are $\Delta H_0^* = 29.8 \pm 0.7$ and $\Delta H_1^* = 23.6 \pm 0.7$ kcal/mol, $\Delta S_0^* = 16.7 \pm 2.0$ and $\Delta S_1^* = -2.1 \pm 1.9$ eu. The quoted errors are standard deviations. The rate constants calculated from these activation parameters agree with the experimentally determined values with an average deviation of 5.0%.

The two-term rate law 2 has been observed for the aquation of $(H_2O)_5CrX^{n+}$ ions whenever X is a basic ligand such as fluoride, acetate, azide, cyanide, or sulfate.[2] This is generally interpreted as (and at least in the case of acetate[7] has been shown to be) the result of a rapid protonation equilibrium preceding rate-determining steps.

$$\mathrm{CrX}^{n+} + \mathrm{H}^+ \overset{1/K_a}{\rightleftharpoons} \mathrm{CrXH}^{(n+1)+} \qquad (3)$$

$$\mathrm{CrX}^{n+} \xrightarrow{k_0} \text{products} \qquad (3a)$$

$$\mathrm{CrXH}^{(n+1)+} \xrightarrow{k_1'} \text{products} \qquad (3b)$$

This mechanism leads to the rate law

$$\frac{-\mathrm{d}\ln(\mathrm{Cr_T})}{\mathrm{d}t} = k_{obsd} = \frac{k_0 + k_1'(\mathrm{H}^+)/K_a}{1 + (\mathrm{H}^+)/K_a}$$

where (Cr_T) represents the total concentration of the starting material in both protonated and unprotonated forms. When $(H^+)/K_A \ll 1$, this reduces to

$$k_{obsd} = k_0 + k_1'(\mathrm{H}^+)/K_a$$

which is the observed rate law with $k_1 = k_1'/K_a$. If X is a multiatomic ligand, it is sometimes difficult to decide which atom of CrX^{n+} is being protonated in equilibrium 3.[7] In the case of the pentaaquo(4-thioanilinium-*S*)chromium(III) ion, the S atom would seem to be the most reasonable site, although protonation at the N atom cannot be ruled out *a priori*. The latter can, however, be eliminated from consideration by the observation that the aquation of the pentaaquo(4-thio(*N*,*N*,*N*-trimethylanilinium)-*S*)chromium(III) ion, in which the nitrogen is coordinatively saturated with three inert methyl groups, is also acid catalyzed. At $\mu = 2.0$ *F* ($NaClO_4$) and 50°, the following first-order rate constants were observed at acid concentrations of 0.101, 0.513, 1.026, and 1.272 *F*, respectively, 1.8×10^{-4}, 2.5×10^{-4}, 2.9×10^{-4}, and 3.9×10^{-4} sec^{-1}. Thus it seems likely that it is the sulfur atom of $(H_2O)_5CrSC_6H_4NH_3^{3+}$ which is protonated in the activated complex corresponding to step 3b. Protonation of thiolato–chromium(III) complexes appears to be a general phenomenon since the rates of Cr–S bond fission in the *O*,*S*-mercaptoacetatobis(ethylenediamine)chromium(III),[21] *N*,*S*-cysteaminebis(ethylenediamine)chromium(III),[21] and *O*,*S*-mercaptoacetatotetraaquochromium(III)[3] ions are all acid catalyzed. Neither the aquation of the $(H_2O)_5CrSH^{2+}$ [20] nor $(H_2O)_5CrSCN^{2+}$ [19] ions is so catalyzed, presumably because H_2S and HSCN are stronger acids than most thiols, and thus coordinated HS^- and SCN^- are more difficult to protonate than coordinated RS^-. In a similar fashion, the fact that k_1 $(= k_1'/K_a)$ for Cr–S bond breaking in *O*,*S*-mercaptoacetatotetraaquochromium(III) is greater than k_1 for pentaaquo(4-thioanilinium-*S*)chromium(III) (see Table II) can be explained in part because aromatic thiols are more acidic, *i.e.*, have larger K_a's, than aliphatic thiols.[22] In addition the 1+ formal charge of the chelated mercaptoacetato complex will favor its protonation relative to the 3+ thioanilinium complex. It should be noted that since the value of k_1 entered in Table II for $(H_2O)_5CrSC_6H_4NH_3^{3+}$ was determined at $\mu = 2.00$ *F* which strongly favors protonation[7] relative to $\mu = 0.25$ *F* at which the mercaptoacetato rate was determined,[3] the difference between these rate parameters determined at a constant ionic strength would be even larger than what is indicated in Table II.

The relative order of k_0 terms for Cr–S bond fission which are listed in Table II may be rationalized in terms of the softness[23] of the sulfur atoms in each ligand. This order is, however, opposite to what one would predict from the proposal[24] that the transition

---

[19] M. Orhanovic and N. Sutin, *J. Amer. Chem. Soc.*, **90**, 4286 (1968); A. Haim and N. Sutin, *ibid.*, **88**, 434 (1966).

[20] M. Ardon and H. Taube, *ibid.*, **89**, 3661 (1967).

[21] C. Weschler and E. Deutsch, manuscript to be submitted.

[22] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. I, Chemical Publishing Co., New York, N. Y., 1958, pp 56–57.

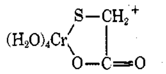
[23] R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

[24] T. W. Swaddle, *ibid.*, **89**, 4338 (1967).

TABLE II

SELECTED RATE CONSTANTS AND ACTIVATION PARAMETERS ASSOCIATED WITH THE RATE LAW

$$\frac{-\mathrm{d}\ln[\mathrm{CrX}^{n+}]}{\mathrm{d}t} = k_0 + k_1(\mathrm{H}^+)$$

CrX^{n+}	μ	10^6k_0, sec^{-1} (25°)	ΔH_0*, kcal/mol	ΔS_0*, eu	10^6k_1, M^{-1} sec^{-1} (25°)	ΔH_1*, kcal/mol	ΔS_1*, eu	Ref
$(H_2O)_5CrSCN^{2+}$	1.0	$59^{a,b}$	23.5 ± 0.3	1.0 ± 0.9	Not obsd			19
$(H_2O)_5CrSC_6H_4NH_3^{3+}$	2.0	4.0^a	29.8 ± 0.7	16.7 ± 2.0	11^a	23.6 ± 0.7	−2.1 ± 1.9	*c*
	0.25	0.6^d			70^d			3
$(H_2O)_5CrN_3^{2+}$	1.0	0.054^a	31.4 ± 0.3	13.5 ± 0.8	0.82^a	23.4 ± 0.2	−7.9 ± 0.6	*e*
$(H_2O)_5CrF^{2+}$	1.0	0.0008^a	28.7 ± 0.6	−3.9 ± 1.8	0.013^a	24.5 ± 0.3	−12.4 ± 0.8	*f*

[a] Calculated using listed values of ΔH* and ΔS*. [b] Sum of aquation (17×10^{-6} sec^{-1}) and isomerization (42×10^{-6} sec^{-1}) reactions. [c] This work. [d] Rate of Cr–S bond fission in opening of chelate ring. [e] T. W. Swaddle and E. King, *Inorg. Chem.*, **3**, 234 (1964). [f] T. W. Swaddle and E. King, *ibid.*, **4**, 532 (1965).

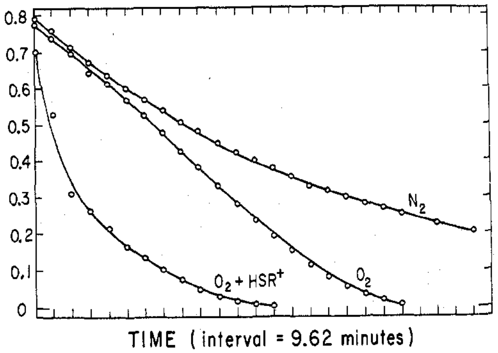


Figure 3.—(OD_t − OD_∞) *vs.* time plots for the aquation of $(H_2O)_5CrSC_6H_4NH_3^{3+}$, first under anaerobic conditions, then equilibrated with oxygen before the run, and finally equilibrated with oxygen and with *p*-aminothiophenol (0.022 *F*) added. All three runs have the following conditions in common: 39.3°, μ = 2.0 *F* ($NaClO_4$), (H^+) = 1.0 *F*, initial concentration of $(H_2O)_5CrSC_6H_4NH_3^{3+}$ 4.3×10^{-3} *F*, kinetics followed at 595 nm.

state of the k_0 term in rate law 2 involves the separation of HX from a hydroxochromium(III) ion. The data in Table II are insufficient to decide this point and further elucidation will have to await a detailed kinetic study of an aliphatic thiol system.

Aerobic Aquation of the Pentaaquo(4-thioanilinium-*S*)chromium(III) Ion.—Under nitrogen, the aquation of the $(H_2O)_5CrSC_6H_4NH_3^{3+}$ ion is typical of the aquation of other pentaaquochromium(III) complexes of weak acid ligands having a pK_a of about 5 (see Table II). However, in the presence of oxygen the mechanism of aquation is drastically altered. This alteration is manifested in Figure 3 which shows (OD_t − OD_∞) *vs.* time plots for identical aquation runs, done first under nitrogen, secondly under a pure oxygen atmosphere, and finally under oxygen with *p*-aminothiophenol added to the reaction solution. The anaerobic run shows typical first-order decay behavior, while the aerobic run shows approximately linear decay over more than 80% of the reaction, indicating zero-order behavior. However, two additional pieces of information show that this decay is not truly zero-order in $(H_2O)_5CrSC_6H_4NH_3^{3+}$, but is the result of an autocatalytic kinetic system. First, the slope of linear aerobic decay plots is a function of the initial concentration of the $(H_2O)_5CrSC_6H_4NH_3^{3+}$ ion. In addition, this slope is always equal to the initial slope of the equivalent anaerobic run (*e.g.*, see Figure 3), indicating that it is chemistry which occurs *during the reaction* that leads to linear decay. Second, when solutions of relatively high concentration of $(H_2O)_5CrSC_6H_4NH_3^{3+}$ (*ca.* 1×10^{-2} *F*) are allowed to aquate in a pure oxygen atmosphere, the resulting (OD_t − OD_∞) *vs.* time plot definitely shows the S shape which is characteristic of autocatalytic reactions.[25] The fact that significant induction periods are not observed in these runs is probably due to the experimental procedure involved in preparing reaction solutions. Presumably the time taken to equilibrate the reaction solutions with air or oxygen, and then bring them to temperature, is of the same order of magnitude as the induction period. The first point of a run (zero time in Figure 3) is usually obtained about 15–20 min after mixing.

Several additional observations serve to define further the chemistry and mechanism of the oxygen catalysis of $(H_2O)_5CrSC_6H_4NH_3^{3+}$ aquation. (1) Aquation of the $(H_2O)_5CrSC_6H_4N(CH_3)_3^{3+}$ ion shows the same aerobic autocatalytic aquation behavior as does the nonmethylated parent compound, indicating that the nitrogen is not participating in the oxygen catalysis. (2) The final products of the aerobic aquation are hexaaquochromium(III) and *p*-aminophenyl disulfide. Blank experiments show that, under the conditions of our experiments, oxygen will readily oxidize *p*-aminothiophenol to *p*-aminophenyl disulfide. (3) The addition of hexaaquochromium(III), *p*-aminophenyl disulfide, or *p*-aminothiophenol to anaerobic aquation reactions has no effect. Likewise the addition of either or both hexaaquochromium(III) and *p*-aminophenyl disulfide has no effect on aerobic aquation reactions and thus neither of these products can be the autocatalytic agent. (4) However, the addition of *p*-aminothiophenol to aerobic aquation reactions has a marked effect which is illustrated in Figure 3. Under these conditions the (OD_t − OD_∞) *vs.* time plot approximates first-order decay, the first-order rate constant being about five times larger than the corresponding anaerobic rate constant when the added mercaptan concentration is about five times that of the chromium complex (and about two times larger when the added mercaptan concentration is about two times that of the chromium complex). This evidence strongly indicates that *p*-aminothiophenol is an essential component of the autocatalytic mechanism observed in the presence of oxygen. (5) If the number of moles of oxygen available to the

---

(25) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, pp 19–20.

reaction mixture is limited, the $(OD_t - OD_\infty)$ *vs.* time plot is linear only until the oxygen is consumed or falls below a critical level. After this point the decay becomes first-order, the calculated rate constant being equal to the comparable anaerobic rate constant. (6) Similarly, linear aerobic decay is only observed when the initial concentration of $(H_2O)_5CrSC_6H_4NH_3^{3+}$ is greater than about 10^{-3} F. If the initial concentration is lowered to 10^{-5} F, the complex then aquates in a first-order manner with a rate constant equal to that observed under nitrogen.

Several mechanisms can be proposed which are consistent with the above observations. One simple example is the following, where R = $-SC_6H_4NH_3$ and waters of hydration are not indicated

$$H^+ + CrSR^{3+} \xrightarrow{k_{N_2}} Cr^{3+} + HSR^+ \qquad (1)$$

$$k_{N_2} = k_0 + k_1(H^+)$$

$$HSR^+ + O_2 \longrightarrow \cdot SR^+ + HO_2 \qquad (4a)$$

$$HSR^+ + HO_2 \longrightarrow \cdot SR^+ + H_2O_2 \qquad (4b)$$

$$HSR\ ^+ H_2O_2 \longrightarrow \cdot SR^+ + \cdot OH + H_2O \qquad (4c)$$

$$HSR^+ + \cdot OH \longrightarrow \cdot SR^+ + H_2O \qquad (4d)$$

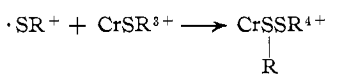
$$H^+ + \cdot SR^+ + CrSR^{3+} \longrightarrow Cr(\cdot SR)^{4+} + HSR^+ \qquad (5)$$

$$Cr(\cdot SR)^{4+} \longrightarrow Cr^{3+} + \cdot SR^+ \qquad (6)$$

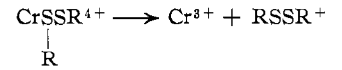
$$\cdot SR^+ + \cdot SR^+ \longrightarrow RSSR^{2+} \qquad (7)$$

In this scheme, the HSR^+ which results from the anaerobic aquation of $CrSR^{3+}$ is oxidized to the free radical $\cdot SR^+$ by molecular oxygen. The reduction products of oxygen, HO_2, H_2O_2, and OH, may very possibly enter into reactions other than 4b, 4c, and 4d, but such complications are not necessary to explain the observed phenomena. Data presented in the next section show that at least hydrogen peroxide does not react with $CrSR^{3+}$ rapidly enough for it to be the dominant catalytic carrier. The radical $\cdot SR^+$ functions as a true catalyst *via* steps 5 and 6 in which $CrSR^{3+}$ is aquated to produce additional HSR^+. Since HSR^+ is the source of $\cdot SR^+$ *via* step 4, this scheme will result in autocatalytic kinetics whenever step 4 is faster than the catalytic cycle created by steps 5 and 6. Step 7 destroys the catalyst and yields the observed disulfide product. In order for this scheme to produce net catalysis of aquation, steps 4, 5, and 6 must each be faster than the rate of aquation under nitrogen (step 1). Thus, when step 4 is slowed by decreasing the concentration of oxygen, or step 5 is slowed by decreasing the concentration of $CrSR^{3+}$, step 1 becomes rate determining and the first-order rates observed under these conditions (equal to the anaerobic aquation rates) are easily explained. Likewise, in the presence of added HSR^+, step 5 is probably rate limiting and $CrSR^{3+}$ disappears by an approximately first-order process, the minor observed deviations from first-order behavior reflecting variations in the concentration of $\cdot SR^+$, which is controlled by competition between steps 4 and 7, during the course of the reaction.

Step 5, which is written as an outer-sphere electron transfer, and step 6 are of course indistinguishable from a mechanism involving a bridged complex[26]



$$\cdot SR^+ + CrSR^{3+} \longrightarrow \underset{\substack{| \\ R}}{CrSSR^{4+}} \qquad (5')$$



$$\underset{\substack{| \\ R}}{CrSSR^{4+}} \longrightarrow Cr^{3+} + RSSR^+ \qquad (6')$$

$$RSSR^+ + H^+ \longrightarrow HSR^+ + \cdot SR^+ \qquad (8)$$

Regardless of the details of the electron transfer, the basic supposition underlying both catalytic mechanisms is that step 6 or 6′ is always faster than step 1; *i.e.*, a free radical is lost from the chromium(III) coordination sphere at a faster rate than is an anion (or actually in this case a zwitterion). This supposition is intuitively reasonable since the Cr–S bond of the free radical complex should be considerably weaker than that of the thiolato complex, and it is also supported by observations made on other inert metal centers. For example, Haim and Taube[27] have reported that a variety of one-electron oxidizing agents induce the aquation of $(NH_3)_5CoI^{2+}$ to $(NH_3)_5CoOH_2^{3+}$, presumably *via* the rate-determining formation of $(NH_3)_5CoI^{3+}$ followed by rapid dissociation of this complex into I· and $(NH_3)_5Co^{3+}$.

Catalysis of Aquation by Oxidants.—Since the remarkable aerobic aquation behavior of the $(H_2O)_5CrSC_6H_4NH_3^{3+}$ ion seemed to be due to the ability of coordinated thiolate to be oxidized, we thought it worthwhile to investigate the efficacy of other oxidants in promoting the aquation of this complex. In general it was found that oxidants are effective in this process, although the reaction of many common oxidizing agents with the $(H_2O)_5CrSC_6H_5NH_3^{3+}$ ion cannot be quantitatively studied because of complications. For example, iron(III) or hypochlorite cause precipitation when added to a solution of $(H_2O)_5CrSC_6H_4NH_3^{3+}$, while cerium(IV) yields deeply colored materials resulting from oxidation of the aniline moiety.[28] However, hydrogen peroxide reacts cleanly and rapidly with the $(H_2O)_5CrSC_6H_4NH_3^{3+}$ ion, yielding hexaaquochromium(III) and *p*-aminophenyl disulfide. In a given experiment this reaction is first-order in complex for over four half-lives; the data in Table III show that the reaction is also first-order in H_2O_2 with a small acid dependence. Thus the empirical form of the rate law is

TABLE III

RATE DATA FOR THE HYDROGEN PEROXIDE INDUCED AQUATION OF THE $(H_2O)_5CrSC_6H_4NH_3^{3+}$ ION[a]

$[H_2O_2]_0$, M	$[H^-]$, M	10^3k_{obsd}, sec^{-1}	$k_{obsd}/[H_2O_2]$, M^{-1} sec^{-1}
0.026	0.050	0.732	0.028
0.138	0.050	3.38	0.024
0.183	0.050	4.87	0.027
0.229	0.050	5.71	0.025
0.275	0.050	6.66	0.024
0.320	0.050	7.86	0.024
0.412	0.050	10.2	0.025
0.275	1.08	22.4	0.081

[a] Conditions: 25°, $\mu = 2.00$ F ($LiClO_4$), initial concentration of $(H_2O)_5CrSC_6H_4NH_3^{3+} = 4.5 \times 10^{-3}$ F, kinetics followed at 595 nm.

$$\frac{-d(CrSR^{3+})}{dt} = A(CrSR^{3+})(H_2O_2)$$

the acid dependence of A not being delineated. This

---

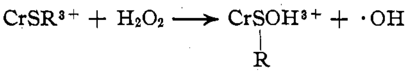
(26) M. Anbar, *Advan. Chem. Ser.*, **49**, 126 (1965).

(27) A. Haim and H. Taube, *J. Amer. Chem. Soc.*, **85**, 495 (1963).

(28) W. H. Richardson, in "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, p 269.

induced aquation may proceed *via* a rate-determining, one-electron, redox reaction (outer sphere as in 9a or inner sphere as in 9b) followed by rapid dissociation of

$$H^+ + CrSR^{3+} + H_2O_2 \longrightarrow Cr(\cdot SR)^{4+} + H_2O + \cdot OH \qquad (9a)$$



$$CrSR^{3+} + H_2O_2 \longrightarrow \underset{\displaystyle R}{CrSOH^{3+}} + \cdot OH \qquad (9b)$$

the coordinated free radical and rapid destruction of radical intermediates.[29] In addition, by measuring initial rates it was possible to show that iron(III) also induces a rapid aquation of the $(H_2O)_5CrSC_6H_4NH_3^{3+}$ ion, this complex disappearing in a first-order manner. Although tested only over a small range of concentrations, the rate law

$$\frac{-d(CrSR^{3+})}{dt} = B(CrSR^{3+})(Fe^{3+})$$

seems to govern this reaction, the acid dependence of B not being delineated. At 25°, $(H^+) = 0.6\ F$, and $\mu = 2.0\ F$ $(NaClO_4)$, B is approximately $3 \times 10^{-2}\ M^{-1}\ sec^{-1}$. The mechanism of this aquation presumably involves the rate-determining redox reaction

$$Fe^{3+} + CrSR^{3+} \longrightarrow Cr(\cdot SR)^{4+} + Fe^{2+} \qquad (10)$$

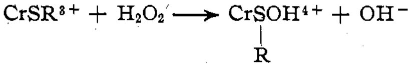
followed by relatively rapid steps 6 and 7.

These observations are all consistent with the general hypothesis that oxidation of coordinated thiolate leads to its labilization, presumably because of the relative lability of coordinated free radicals. Hydrogen peroxide and iron(III), but not molecular oxygen, are able to perform this oxidation directly. Molecular oxygen seems to require an intermediate such as $\cdot SR^+$ or iron(III) to mediate the electron transfer (addition of iron(II) to aerobic aquation runs leads to first-order disappearance of $(H_2O)_5CrSC_6H_4NH_3^{3+}$). This observation should be of some importance in limiting the vast number of mechanisms that currently may be proposed to explain the metal ion catalyzed autoxidation of thiols.[5]

Acknowledgments.—Funds for this work were provided by ARPA and by a DuPont Young Faculty Grant. The authors also express their appreciation to J. Halpern for helpful discussions, and to D. Ford for preparation of the 4,4′-dithiobis(*N*,*N*,*N*-trimethylanilinium) cation.

---

[29] In light of the general inertness of H_2O_2 to one-electron reduction, it is also possible that the initial rate-determining step involves a two-electron change, *i.e.*, nucleophilic displacement of oxygen by sulfur (9c). Presumably



$$CrSR^{3+} + H_2O_2 \longrightarrow \underset{\displaystyle R}{CrSOH^{4+}} + OH^- \qquad (9c)$$

this oxidized product would aquate rapidly and the species RSOH thus liberated would convert a coordinated thio ligand to a disulfide. A coordinated disulfide might again be expected to aquate fairly rapidly. The authors are grateful to Professor H. Taube for suggesting this alternate mechanism.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO,
BOULDER, COLORADO 80302

Kinetic and Equilibrium Studies of Ethylene Glycol–Chromium(III) Species in Acidic Ethylene Glycol–Water Solutions[1]

BY HOMER B. KLONIS AND EDWARD L. KING*

Received June 6, 1972

In acidic aqueous ethylene glycol (G), chromium(III) forms two different monoglycol complexes; in one, glycol is a monodentate ligand and in the other it is a bidentate ligand. The interconversion of these species is very much faster than the reaction of glycol with hexaaquochromium(III) ion. Parameters evaluated in this study are the following: (a) the equilibrium quotients $Q_I = [Cr(OH_2)_5G^{3+}]a_w/[Cr(OH_2)_6^{3+}]a_g = 0.35$ (60°) and $Q_{II} = [Cr(OH_2)_4G^{3+}]a_w/[Cr(OH_2)_5G^{3+}] = 0.17 \pm 0.06$ (15–30°); and (b) the rate laws and rate coefficients: $d[Cr(OH_2)_5G^{3+}]/dt = k_1[Cr(OH_2)_6^{3+}]a_g - k_{-1}[Cr(OH_2)_5G^{3+}]a_w$ with $k_1 = 9.0 \times 10^{-4}\ sec^{-1}$ (60°), 7.5×10^{-5} (40°), and $d[Cr(OH_2)_4G^{3+}]/dt = k_2[Cr(OH_2)_5G^{3+}] - k_{-2}\cdot[Cr(OH_2)_4G^{3+}]a_w$, with $10^4k_2 = 3.2 \pm 1\ sec^{-1}$ (15°), 5.6 ± 1 (20°), 9.5 ± 2 (25°), and 11.2 ± 4 (30°). Light absorption in the visible region by the chelated species is appreciably greater than by the nonchelated species. Species containing two (and more) coordinated glycol molecules were not isolated, but there is spectral evidence for the presence of such species in solutions with a high concentration of glycol ($Z > 0.9$).

Although ethylene glycol[2] is structurally similar to ethylenediamine, complexes of glycol with transition metal ions have been studied less thoroughly than the amine complexes. Glycol is much less basic than ethylenediamine, but it should show coordination with chromium(III) ion in the binary glycol–water solvent system, as methanol[3,4] and ethanol[4,5] show such coordination to chromium(III) ion in their binary solvent systems with water. The present paper deals with both equilibrium and kinetic aspects of the coordination of glycol with chromium(III) ion. Of particular interest is the question of whether both species with monodentate glycol and bidentate glycol have similar stability. Evidence will be presented to show that both species have appreciable stability; the relative concentration of the two species is a function of the activity of water.

Experimental Details and Results

Reagents.—Reagent grade chemicals were used without additional purification unless otherwise noted. The ethylene glycol

---

[1] Taken in part from the Ph.D. thesis of H. B. Klonis, University of Colorado, 1971. This work was supported in part by National Science Foundation Grant GP 7185-X.

[2] Hereafter ethylene glycol will be called simply glycol; in chemical formulas it will be represented as G.

[3] J. C. Jayne and E. L. King, *J. Amer. Chem. Soc.*, **86**, 3989 (1964).

[4] C. C. Mills, III, and E. L. King, *ibid.*, **92**, 3017 (1970).

[5] D. W. Kemp and E. L. King, *ibid.*, **89**, 3433 (1967).