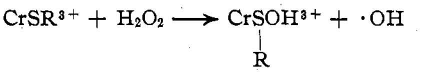
induced aquation may proceed *via* a rate-determining, one-electron, redox reaction (outer sphere as in 9a or inner sphere as in 9b) followed by rapid dissociation of

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



$$CrSR^{3+} + H_2O_2 \longrightarrow Cr\underset{\displaystyle R}{\underset{|}{S}}OH^{3+} + \cdot OH$$

(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

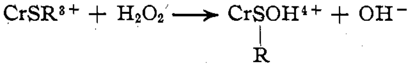
$$Fe^{3+} + CrSR^{3+} \longrightarrow Cr(\cdot SR)^{4+} + Fe^{2+} \qquad (10)$$

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



$$CrSR^{3+} + H_2O_2 \longrightarrow Cr\underset{\displaystyle R}{\underset{|}{S}}OH^{4+} + OH^-$$

(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).

TABLE I

EQUILIBRIUM VALUES OF $\bar{n}$ AT 40 AND 60°, $[\mathrm{Cr^{III}}] = 9.9 \times 10^{-3}$ *M*,[a] $[\mathrm{H^+}] = 0.103$ *M*[a]

Z	$\bar{n}$	*Z*	$\bar{n}$	*Z*	$\bar{n}$
40°		60°		60°	
0.335	0.160 ± 0.003 (4)[b]	0.270	0.176 ± 0.011 (4)	0.733	0.677 ± 0.005 (8)
0.539	0.331 ± 0.004 (4)	0.335	0.217 ± 0.010 (6)	0.797	0.775 ± 0.010 (3)
0.672	0.486 ± 0.006 (4)	0.342[c]	0.233 ± 0.009 (4)	0.845	0.881 ± 0.005 (8)
0.845	0.773 ± 0.010 (4)	0.453	0.310 ± 0.008 (4)	0.881	0.950 ± 0.006 (9)
60°		0.539	0.397 ± 0.006 (6)	0.906[c]	0.963 ± 0.006 (3)
0.100	0.056 ± 0.004 (3)	0.576	0.450 ± 0.012 (8)	0.913	0.991 ± 0.015 (14)
0.143	0.082 ± 0.004 (4)	0.612[c]	0.522 ± 0.004 (4)	0.960	1.010 ± 0.006 (8)
0.148	0.087 ± 0.006 (3)	0.617	0.518 ± 0.004 (6)	0.976	0.989 ± 0.014 (8)
0.200	0.111 ± 0.005 (5)	0.672	0.570 ± 0.008 (4)	0.980[c]	1.020 ± 0.003 (3)
0.266	0.161 ± 0.006 (5)	0.718	0.642 ± 0.010 (4)	0.988[d]	1.043 ± 0.003 (2)

[a] Perchlorate is the anion present. [b] Uncertainty is average deviation among duplicate analysis on one to five equilibrated solutions of the same composition. The number in parentheses is the number of analyses performed. [c] $[\mathrm{Cr^{III}}] = 4.9 \times 10^{-3}$ *M*, $[\mathrm{H^+}] = 0.051$ *M*. [d] $[\mathrm{Cr^{III}}] = 2.5 \times 10^{-3}$ *M*, $[\mathrm{H^+}] = 0.026$ *M*.

was Matheson Coleman and Bell "Chromatoquality Grade." Hexaaquochromium(III) perchlorate was prepared from reagent grade chromium(VI) oxide as described earlier.[4] Aquopentaamminecobalt(III) perchlorate was prepared from carbonatopentaamminecobalt(III) nitrate[6] by treatment with dilute aqueous perchloric acid.[7] The spectrum of a solution of the salt so prepared agreed with that reported.[7]

Solutions of *cis*-diaquotetraamminecobalt(III) ion were prepared by acidification of solutions of carbonatotetraamminecobalt(III) sulfate, which was prepared using a published procedure.[8]

Analyses.—Analysis for glycol was based upon its oxidation to carbon dioxide by chromium(VI) in 9–10.5 *M* sulfuric acid.[9] The chromium(III) produced was determined spectrophotometrically at 610 nm, where it absorbs strongly compared to chromium(VI). In 10.5 *M* sulfuric acid, the molar absorptivity for chromium(III) at 610 nm is 21.4 l. $\mathrm{mol^{-1}\ cm^{-1}}$; the molar absorptivity for chromium(VI) in this solvent at 610 nm ranges from 1.32 to 1.20 l. $\mathrm{mol^{-1}\ cm^{-1}}$ (expressed on a monomer basis) as the concentration of chromium(VI) varies from 0.0067 to 0.0233 *M* (expressed on a monomer basis). This variation, due presumably to the shifting of the monomer–dimer chromium(VI) equilibrium,[10] was taken into account. The oxidation was carried out at 80° for 1 hr, during which period the glycol–chromium(III) species aquate completely. The analysis for glycol bound to cobalt(III) was essentially the same; at 610 nm the molar absorptivity for aquopentaamminecobalt(III) is 3.22 l. $\mathrm{mol^{-1}\ cm^{-1}}$ in 11 *M* sulfuric acid; for *cis*-diaquotetraamminecobalt(III) ion, the molar absorptivity at this wavelength is 12.90 l. $\mathrm{mol^{-1}\ cm^{-1}}$. Chromium analyses were performed spectrophotometrically on solutions containing chromate ion,[11] this species having been formed from chromium(III) species by oxidation with alkaline hydrogen peroxide.

Preparation and Composition of Solutions.—Solutions containing perchloric acid, chromium(III) perchlorate, water, and glycol were prepared by a combination of volumetric and gravimetric techniques thereby allowing calculation of the mole fraction composition of the solvent and the molarities of the solutes. In calculation of the mole fraction of each solvent component, only the solvent components were taken into account. For solutions with mole fraction of glycol (*Z*) greater than 0.90, a correction was made in calculating the number of moles of water by assuming 1 mol of water was bound per hydrogen ion. (It was assumed that hydronium ion is randomly solvated by water and glycol.) In addition the solvent composition was corrected for 4 mol of water bound per mole of chromium(III) in this composition range, it being assumed that in the predominant chromium(III) species 1 mol of bidentate glycol is coordinated. (These corrections are small; in addition, uncertainties regarding the activity of water and the possible presence of diglycolchromium(III) species in the glycol-rich electrolyte solutions leads in quantitative correlations to assignment of low weight to the data from such solutions.)

The Glycol–Water System.—The glycol–water system is close to ideal.[12] Activity coefficients used in calculations in the present work were taken from the study by Fogg[12a] at 1 atm pressure and variable temperature. For glycol, $1.00 > \gamma > 0.96$ at all compositions; for water, $1.00 > \gamma > 0.90$ at $Z < 0.75$.

$\bar{n}$ Experiments.—The average number of glycol molecules bound per chromium(III) ion ($\bar{n}$) was determined as a function of solvent composition (Z = 0.100–0.988 at 60°; Z = 0.335–0.845 at 40°). At 60°, equilibration times varied from several hours to several days. (Later kinetic experiments, to be described, showed the half-time for equilibration at this temperature to be ~6 min for $Z = 0.035$ and ~19 min for $Z = 0.98$.) At 40°, the equilibration times varied from 2 to 16 days; the half-time for equilibration at this temperature varied from ~1.4 hr at Z = 0.20 to ~4 hr at Z = 0.87. Analysis for the average glycol content of the chromium(III) species was carried out after first separating chromium(III) from the mixed solvent in which it was equilibrated by a column ion-exchange procedure similar to that used in studies on other systems.[3-5] Before adding the equilibrated solution to a batch of resin (Dowex 50W X-8 50–100 mesh), it was diluted fivefold with chilled aqueous 0.1 *M* perchloric acid. The resin containing chromium(III) then was transferred to the top of a 3-cm column of resin for rinsing and elution. The glycol-containing solvent was rinsed away with 0.02 *M* sulfuric acid, and 3 *M* sulfuric acid was used to elute quantitatively (97 ± 2%) the solvated chromium(III) ion. This procedure was carried out at ~5°, and the loading of the resin, rinsing, and elution required 5–6 hr. The values of $\bar{n}$ are given in Table I.

Similar studies of the coordination of glycol to the pentaamminecobalt(III) and tetraamminecobalt(III) moieties were carried out at 60° in solutions with $\sim 10^{-2}$ *M* $\mathrm{Co^{III}}$, 0.01–0.1 *M* perchloric acid. The equilibrium values of $\bar{n}$ for binding of glycol to pentaamminecobalt(III) are the following (given as Z, $[\mathrm{H^+}]$, $\bar{n}$): 0.82, 0.12, 0.038; 0.86, 0.012, 0.059; 0.927, 0.12, 0.108; and 0.968, 0.012, 0.225. For tetraamminecobalt(III) the data (given as Z, $[\mathrm{H^+}]$, $\bar{n}$) are the following: 0.486, 0.10, 0.079; 0.676, 0.10, 0.21; 0.823, 0.10, 0.45; and 0.961, 0.090, 0.94. Analysis showed that ammonia was not lost from the coordination shell of cobalt(III) during equilibration at 60° in the mixed solvent system.

Separation of Species.—Aquochromium(III) ion and glycolchromium(III) ion present in equilibrated solutions were separated from one another by an ion-exchange procedure. For these experiments Dowex 50W-X12 200–400 mesh resin was used; the column length was 60 cm, and the entire procedure required 21–35 hr. The eluting agent was ~2 *M* sulfuric acid. Figure 1 shows the elution curve from one experiment. In this and all similar elutions, only two species were separated. The analyzed values of $\bar{n}$ for the recovered chromium were 0.00 ± 0.05 and 1.00 ± 0.02 for the first and second peaks, respectively. The recovery of chromium(III) in the longer elution procedures of these separation experiments was 93 ± 3%. The concentrations of glycolchromium(III) ion (represented as $\mathrm{CrG^{3+}}$) relative to aquochromium(III) in the solutions analyzed by these methods were the following (given as Z, $([\mathrm{CrG^{3+}}]/[\mathrm{Cr^{+3}}])$): 0.34, 0.205; 0.54, 0.54; 0.73, 1.27; 0.95 (two experiments), 5.45; and 0.98, 19. Values of $\bar{n}$ calculated from these ratios are slightly lower

---

(6) F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 171 (1953).

(7) R. C. Splinter, S. J. Harris, and R. S. Tobias, *Inorg. Chem.*, **7**, 897 (1968).

(8) G. Brauer, "Handbuch der Preparativen Anorganischen Chemie," F. Enke, Stuttgart, 1954, p 1147.

(9) R. Sargent and W. Riemann, III, *Anal. Chim. Acta*, **14**, 381 (1956).

(10) J. Y. Tong and E. L. King, *J. Amer. Chem. Soc.*, **75**, 6180 (1953).

(11) G. W. Haupt, *J. Res. Nat. Bur. Stand.*, **48**, 414 (1952).

(12) (a) E. Fogg, Ph.D. Thesis, University of Pennsylvania, 1953; (b) H. M. Trimble and W. Potts, *Ind. Eng. Chem.*, **27**, 66 (1935); (c) B. C. Y. Lu, *ibid.*, **52**, 871 (1960).

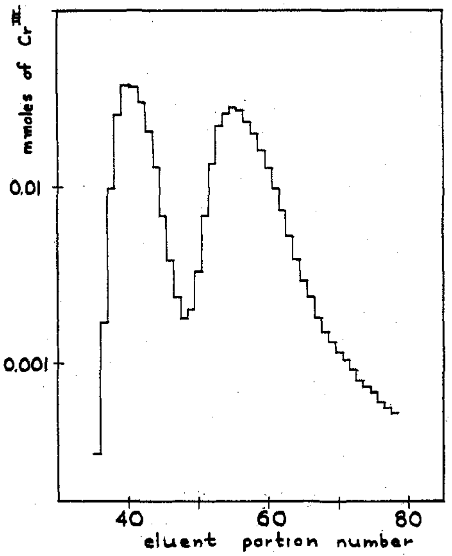


Figure 1.—Elution profile of chromium(III) equilibrated in solution with $Z = 0.73$ ($[Cr^{III}] = 10^{-2}$ M, $[H^+] = 0.103$ M). Eluting agent 2.16 M H_2SO_4; Dowex 50W-X12, 200–400 mesh resin; each fraction 3.3 ml.

than values obtained in the faster column procedures for evaluation of $\bar{n}$. In the longer lasting ion-exchange column separation experiments, some aquation of glycolchromium(III) ion may occur, thereby giving a smaller amount of this species and a smaller derived value of $\bar{n}$. In addition, diglycolchromium(III) species may be present at low concentrations; these species may not survive the longer separation procedure even though they survive partially and were recovered in the $\bar{n}$ experiments.

Spectral Determinations.—Several different types of spectral determinations were informative. The spectrum of an equilibrated solution with $Z = 0.900$ ($[H^+] = 0.103$) has absorption maxima at 430 nm ($\bar{a} = 34.3$ l. mol^{-1} cm^{-1}) and 580 nm ($\bar{a} = 24.3$ l. mol^{-1} cm^{-1}). The value of $\bar{n}$ in this solution is 0.96. The spectrum of monoglycolchromium(III) ion in aqueous 2.6 M perchloric acid at room temperature has absorption maxima at 410 nm ($\bar{a} = 17.6$ l. mol^{-1} cm^{-1}) and 577 nm ($\bar{a} = 15.1$ l. mol^{-1} cm^{-1}). If the equilibrated solution with $\bar{n} \cong 0.96$ contains only a slight amount of diglycolchromium(III) ion, these two solutions, each containing species in which one glycol molecule is coordinated per chromium(III) ion, must contain two (or more) species in different relative amounts because of the dramatic differences in the spectra.

The spectra of a series of equilibrated solutions of varying Z ($Z = 0$–0.976, $[H^+] = 0.103$ M) were measured at 60°. These data do not conform to the isosbestic point principle,[13] indicating that more than two species are present.

Values of $\bar{n}$ were known for the solutions with measured spectra and the contribution to the light absorption by aquochromium(III) can be calculated.[14] The data were converted to apparent values of the molar absorptivity of monoglycolchromium(III) ion, a_1

$$a_1 = \frac{\bar{a} - (1 - \bar{n})a_0}{\bar{n}}$$

in which $\bar{a} = (\log I_0/I)/[Cr^{III}]b$, with ($[Cr^{III}]$ = stoichiometric molarity of chromium(III) and b = cell length. The calculated values of a_1 are the following (given as Z, a_1 (420 nm), a_1 (440 nm)): 0.340, 23.2, 17.7; 0.479, 24.4, 19.7; 0.545, 24.6, 20.6; 0.613, 25.3, 21.2; 0.713, 27.0, 22.7; 0.799, 29.4, 26.0; 0.846, 31.3, 29.0; 0.917, 36.4, 37.1; and 0.956, 40.4, 45.0. (Since appreciable diglycolchromium(III) species are present in the two solutions with highest Z, these calculated values of a_1 are fictitious.)

Kinetic Experiments.—The rate of approach to equilibrium in glycol-containing solutions which contained initially only hexaaquochromium(III) ion was studied at 40 and 60°. These experiments were performed by measuring either the value of $\bar{n}$ or the light absorption as a function of time. The approach to equilibrium was nicely first order in each experiment. (At 60°, the reaction was followed to greater than 99% completion; at 40°, the extent of reaction followed ranged from 30 to 75%.) Values of k (defined $k \equiv (d \ln (P - P_\infty))/dt$, with $P = \bar{n}$ or log (I_0/I)) are presented in Table II.

TABLE II

RATE OF APPROACH TO EQUILIBRIUM IN COORDINATION OF CHROMIUM(III) BY GLYCOL,[a] $[H^+] = 0.10$ M, $[Cr^{III}] = 1.0 \times 10^{-2}$ M

Z	10^4k, sec^{-1}	Z	10^4k, sec^{-1}
40.0 ± 0.05°		60.0 ± 0.05°	
0.200	1.35	0.335	13.0
0.335	1.18	0.453	11.3
0.539	0.895	0.539	10.0
0.617	0.672	0.539	9.2[b]
0.871	0.477	0.617	7.4
		0.617	7.3[b]
60.0 ± 0.05°		0.730	5.8
0.035	19.2	0.797	5.65
0.053	18.5	0.956	5.45
0.070	19.0	0.976	5.34
0.100	18.0		
0.200	17.0		

[a] Molar absorptivity studied unless otherwide noted. [b] Values of $\bar{n}$ followed as function of time.

TABLE III

THE RATE OF APPROACH TO EQUILIBRIUM IN REACTION 2,[a] $[H^+] = 0.10$ M

15.0°		20.0°		25.0°		30.0°	
Z	$10^3k'$	Z	$10^3k'$	Z	$10^3k'$	Z	$10^3k'$
0.285	1.68	0.230	2.96	0.125	5.35[d]	0.325	6.45
0.491	1.30	0.238	3.06	0.230	4.46[d]	0.493	5.27
0.618	1.13	0.245	2.98	0.245	4.46[d]	0.619	4.46
0.731	0.91	0.365	2.54	0.392	3.80	0.712	3.82
0.796	0.775	0.476	2.23	0.493	3.60	0.900	1.72[c]
0.967	0.275[c]	0.593	1.85	0.619	2.90	0.906	1.77[b]
		0.722	1.54	0.712	2.46		
		0.800	1.22	0.828	1.89		
		0.955	0.635[c]	0.900	1.33[c]		
		0.955	0.622[b]	0.975	0.816[c]		
		0.975	0.60[c]				

[a] Unless otherwise noted the initially equilibrated solution had $Z = 0.96$, $[H^+] = 0.103$; this was diluted with aqueous 0.103 M perchloric acid to give the composition given above. The wavelength studied was 423 nm. Dimensions of k', sec^{-1}. [b] Experiment in which Z was increased by addition of an equal volume of pure glycol to a solution with $Z = 0.88$, $[H^+] = 0.206$, previously equilibrated at 60°. [c] Experiment in which a solution initially equilibrated at 60° and then quenched at −15° for 1–2 days was brought to the temperature in question. The wavelength studied was 270 or 285 nm. [d] Wavelength studied 270 nm.

Kinetic experiments of another type also were performed. If an equilibrated solution is diluted with water or glycol to change the value of Z or if an equilibrated solution which had been stored at −15° is warmed to the temperature in question, a relatively rapid change in light absorption occurs. The rate of this change is much greater than the rate of establishment of true equilibrium. The approach to this new quasiequilibrium was studied at 15, 20, 25, and 30°; in most experiments, the light absorption at 423 nm was measured. Plots of ln $(A_t - A'_\infty)$ *vs.* time were nicely linear over >3 half-lives. Values of A'_∞ were measured at times long compared to $t_{1/2}$ for this rapid transformation but short compared to the time required for complete equilibration. The results of these experiments are presented in Table III. In addition, a series of seven experiments was done in which portions of a previously equilibrated solution ($Z = 0.956$, $[H^+] = 0.103$) were diluted with an equal volume of various perchloric acid–lithium perchlorate solutions to give a series of solutions with $Z \cong 0.24$, $I = 1.07$ M, and varying acidity. The observed values of k'

---

(13) J. Brynestead and G. P. Smith, *J. Phys. Chem.*, **72**, 296 (1968).

(14) The molar absorptivity of aquochromium(III) ion (a_0) shows a very mild medium effect as the solvent composition is changed. The change is inappreciable except at high values of Z, where the uncertainty in the value of a_0 has no appreciable influence on the calculated value of a_1.

determined at 20° showed no dependence upon [H$^+$]; from [H$^+$] = 0.055 to 1.05 *M*, $10^3k' = 2.75 \pm 0.06$ sec^{-1}. (The stated uncertainty is the average difference between the individual values and the average value.)

Experiments also were done in which a previously equilibrated solution was diluted with aqueous acetone, and the approach to the new quasiequilibrium was followed at 25°. For $Z = 0.349$ and mole fraction of water = 0.331, $10^3k' = 2.61$ sec^{-1}; for $Z = 0.272$ and mole fraction of water = 0.214, $10^3k' = 2.02$ sec^{-1}.

Interpretation of Results

Values of $\bar{n}$ appreciably greater than 1.0 have not been observed, and diglycolchromium(III) species have not been isolated from equilibrated solutions by the ion-exchange procedure. Based upon correlations of the spectral data, however, it seems likely that diglycolchromium(III) species are present in the solutions of highest Z ($Z > 0.9$). Interpretation of the data for $Z < 0.9$ will be made in terms of reactions involving only aquochromium(III) ion and monoglycolchromium(III) species. These reactions are

$$\mathrm{Cr(OH_2)_6^{3+} + G \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cr(OH_2)_5G^{3+} + H_2O} \qquad (1)$$

$$\mathrm{Cr(OH_2)_5G^{3+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Cr(OH_2)_4G^{3+} + H_2O} \qquad (2)$$

$$\mathrm{Cr(OH_2)_6^{3+} + G = Cr(OH_2)_4G^{3+} + 2H_2O} \qquad (3)$$

(Whether glycol (G) is acting as a monodentate or a bidentate ligand follows from the number of water molecules specified in the coordination shell of chromium(III).) Reactions 1 and 2 will be used in the discussion of both kinetics and equilibrium, and reaction 3 will be used only in the discussion of equilibrium. In quantitative correlations of the data, activities of the solvent components will be assumed to be the same as in electrolyte-free solutions. The ratio of activity coefficients of chromium(III) species and transition states of charge 3+ will be assumed to be independent of solvent composition. This is equivalent to the assumption that equilibrium quotients and rate coefficients do not depend upon solvent composition.

The $\bar{n}$ data are not consistent with only reaction 1 or reaction 3 being the predominant equilibrium. If reaction 1 was the only reaction which occurred, the quotient $\{\bar{n}a_w/((1 - \bar{n})a_g)\}$ would be constant. The values for 60° are relatively constant (0.544 ± 0.013) in the range $Z = 0.10$–0.54 ($\bar{n} = 0.056$–0.397), but above $Z = 0.54$ the value increases; for $Z = 0.797$, 0.845, and 0.881, the values are 0.76, 1.08, and 2.11, respectively. On the other hand for aquopentaamminecobalt(III) ion, which can only form monodentate species, the value of this quotient is approximately constant ($(7.5 \pm 0.5) \times 10^{-3}$) over the solution composition range studied ($Z = 0.82$–0.97, $\bar{n} = 0.038$–0.225). If reaction 3 was the only reaction which occurred, the quotient $\{\bar{n}a_w^2/((1 - \bar{n})a_g)\}$ would be constant. The values of this quotient for the 60° data vary by a factor of approximately 4. For *cis*-diaquotetraamminecobalt(III) ion, each of the quotients being considered varies by a factor of approximately 4. These calculations using $\bar{n}$ data, as well as other observations, argue that both reactions 1 and 2 must be considered in interpretation of the data.

The data which are interpreted most simply are the rates of reequilibration of diluted solutions. On the time scale of these experiments, reaction 1 does not reequilibrate with dilution. The rate coefficient k', values of which are given in Table III, is expected to show the dependence $k' = k_2 + k_{-2}a_w$ if this relatively rapid change is due to reaction 2. Figure 2 shows plots of the data; the derived values of k_2 and k_{-2} are the following (given as t, 10^3k_2 (sec^{-1}), 10^3k_{-2} (sec^{-1})): 15°, 0.32 ± 0.1, 2.0 ± 0.3; 20°, 0.56 ± 0.1, 3.2 ± 0.3; 25°, 0.95 ± 0.2, 4.8 ± 0.4; and 30°, 1.12 ± 0.4, 8.2 ± 1. Values of the quotient k_2/k_{-2} provide the value of Q_{II}; these values are the following (given as t, k_2/k_{-2}): 15°, 0.16 ± 0.08; 20°, 0.18 ± 0.05; 25°, 0.20 ± 0.05; and 30°, 0.14 ± 0.06. The values do not show a monotonic trend, and they are within experimental error of one another. The experimental uncertainty is large, however, and a value of ΔH_{II} between +6 and −6 kcal mol^{-1} would be consistent with the data. Equilibrium in reaction 2 is shifted to the right by increasing the temperature, so a value of $\Delta H_{II} = +3$ kcal mol^{-1} will be assumed in extrapolating values of k_2/k_{-2} to higher temperatures. This extrapolation gives $Q_{II} = 0.30$ at 60° and 0.22 at 40°.

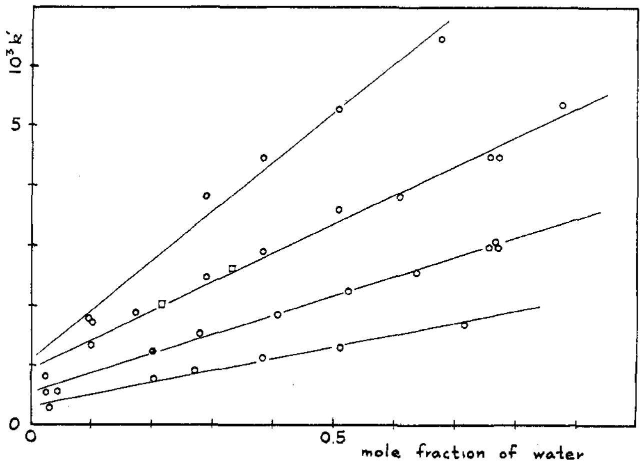


Figure 2.—Dependence of k' upon water content of solution. (The activity of water is approximately equal to the mole fraction of water for $Z < 0.75$.) The four sets of data are for (reading from top to bottom) 30, 25, 20, and 15°. The square points are for the water–glycol–acetone solutions. The straight lines correspond to the parameters given in the text.

The enthalpy of activation associated with k_2 is 15.3 kcal mol^{-1}.

Figure 2 shows also that the data obtained in water–glycol–acetone solutions are correlated in the same manner. If the relatively rapid reequilibration upon dilution was due to conversion of diglycolchromium(III) ion to monoglycolchromium(III) ion, the value of k' would not be a linear function of the activity of water.

With the value of Q_{II} estimated for 60 and 40°, the equilibrium values of $\bar{n}$ obtained at these temperatures can be interpreted to obtain the values of Q_I. Rearrangement of the relationship

$$\frac{\bar{n}}{(1 - \bar{n})}\frac{a_w}{a_g} = Q_I + Q_IQ_{II}a_w^{-1}$$

which is derived from the definition of $\bar{n}$ in terms of species concentrations gives

$$Q_I = \left\{\frac{\bar{n}}{(1 - \bar{n})}\frac{a_w}{a_g}\right\}\Big/(1 + Q_{II}a_w^{-1})$$

The weighted average value of Q_I for 60° calculated in this way is 0.35 ± 0.03. (In arriving at this value of Q_I, data for $Z = 0.100$–0.845 were used with values of $\bar{n}/(1 - \bar{n})$ weighted inversely to their estimated uncertainty. The uncertainty given with Q_I is the weighted average difference between the individually calculated values of Q_I and the weighted average, 0.35.) When the limited data obtained at 40° are treated in this way one obtains $Q_I = 0.39 \pm 0.02$.

Using the parameters for 60°, $Q_I = 0.35$ and $Q_{II} = 0.30$, one calculates values of $\bar{n}$ which have an average deviation of 0.016 units from the observed value over the range $Z = 0.100$–0.845. Using the values for 40°, $Q_I = 0.39$ and $Q_{II} = 0.22$, the average difference between the observed and calculated values of $\bar{n}$ is 0.009 units.[15]

In the approach to complete equilibrium, reaction 2 stays essentially at the equilibrium as reaction 1 occurs. Under such circumstances the rate coefficient for the establishment of equilibrium is given by

$$k = k_1 a_g + k_{-1} a_w \left\{ \frac{a_w}{a_w + Q_{II}} \right\}$$

in which the last factor on the right side of the equation is the fraction of glycolchromium(III) ion in which glycol is acting as a monodentate ligand. If we accept the values of Q_I and Q_{II} already established, this equation involves only a single unknown k_1; the equation appropriately rearranged is

$$k_1 = k \bigg/ \left(a_g + \frac{a_w^2}{Q_I(a_w + Q_{II})} \right)$$

The values of k_1 calculated using this equation with values of k for 60° given in Table II and $Q_I = 0.35$ and $Q_{II} = 0.30$ are the following (given as Z, $10^4 k_1$ (sec^{-1})): 0.035, 9.0; 0.053, 8.8; 0.070, 9.1; 0.100, 8.9; 0.200, 9.2; 0.335, 8.0; 0.453, 8.0; 0.539, 7.5; 0.617, 6.3; 0.730, 5.6; 0.797, 5.8; 0.956, 5.6; and 0.976, 5.4. Using the values of k for 40° and $Q_I = 0.39$ and $Q_{II} = 0.22$, the calculated values of k_1 are the following (given as Z, $10^5 k_1$ (sec^{-1})): 0.200, 7.5; 0.335, 7.4; 0.539, 6.9; 0.617, 5.7; and 0.871, 5.0. The activation enthalpy associated with the values of k_1 obtained at low Z (60°, 9.0×10^{-4} sec^{-1}; 40°, 7.5×10^{-5} sec^{-1}) is 25.2 kcal mol^{-1}.

The observed dependence of a_1 upon the solvent composition can be attributed to the varying relative amounts of species containing glycol in the monodentate form ($Cr(OH_2)_5G^{3+}$) and the bidentate form ($Cr(OH_2)_4G^{3+}$). If this is the case, the dependence of a_1 upon solvent composition is

$$a_1 = \frac{a_w a_{51} + Q_{II} a_{41}}{a_w + Q_{II}}$$

in which a_{51} and a_{41} are the molar absorptivity values for $Cr(OH_2)_5G^{3+}$ and $Cr(OH_2)_4G^{3+}$, respectively, and a_w is the activity of water. Although the spectral data can be used to evaluate simultaneously the values of a_{51}, a_{41}, and Q_{II}, it seems preferable to accept the value of Q_{II} extrapolated to 60° from values derived from the rate of equilibration in reaction 2 at 15–30° ($Q_{II} = 0.30$) and use the spectral data to obtain values of a_{51} and a_{41}. The values of a_{51} and a_{41} so obtained using data from $Z = 0.340$–0.900 are the following (given as λ (nm), a_{51}, a_{41}): 400, 17.2, 28.8; 410, 17.9, 33.9; 420, 15.7, 38.1; 430, 12.9, 39.2; 440, 8.43, 37.9; 450, 4.95, 34.4; 580, 13.7, 27.0; and 610, 2.65, 16.14 l. cm^{-1} mol^{-1}. Using these values of a_{51} and a_{41} and $Q_{II} = 0.30$, one can calculate values of a_1; the differences between the experimental and calculated values at the several wavelengths are the following (given as λ (nm), diff): 400, 1.0%; 410, 1.1%; 420, 1.7%; 430, 2.8%; 440, 2.6%; 450, 4.2%; 580, 1.4%; 610, 5.4%. Both the observed values of $\bar{a}$ and the derived values of a_1 exceed the calculated values of a_{41} at $Z \geqslant 0.957$. This demonstrates that species involving more than one glycol molecule contribute to the light absorption of such solutions.

Discussion

The interpretation of several different types of data in terms of reactions 1 and 2 has been made in the framework of an assumption of constant ratios of appropriate activity coefficients of species and transition states. These assumptions probably are not strictly correct, but they cannot be checked more directly by available methods. The failure of the finally derived quantity k_1 to be independent of medium is undoubtedly a consequence of these assumptions.

After application of the appropriate statistical factor,[16] the equilibrium quotient Q_I ($Q_I(\text{cor}) = (1/12)Q_I = 0.029$ at 60°) can be compared with equilibrium quotients for the coordination to chromium(III) ion of methanol ($Q_I(\text{cor}) = 0.11$ at 60°)[3,4] and ethanol ($Q_I(\text{cor}) = 0.070$ at 75°, extrapolated to pure ethanol).[5]

This comparison has a faulty basis since it includes, of course, the effect of interactions in the pure liquid organic components.[17] (The standard state for each solvent component is the pure liquid.) This factor is omitted if one compares equilibrium quotients for the reactions

$$Cr(OH_2)_6^{3+} + ROH(g) = Cr(OH_2)_5(OHR)^{3+} + H_2O(l)$$

For these reactions, the values of $Q_I(\text{cor})$ at 60° are the following: glycol, 14.7; methanol, 0.13; and ethanol, 0.15. The greater stability of the glycolchromium(III) species calculated on this basis is due undoubtedly to the hydrogen bonding interactions between the solvent and the free hydroxyl group of monodentate glycol, a structural feature not present in the methanol and ethanol species.

The chromium(III)–glycol complexes are very different from the chromium(III)–ethylenediamine complexes with respect to the relative stability of the monodentate and bidentate forms. For the ligand with the greater coordinating ability, ethylenediamine, the monodentate form is present in solution only under conditions where the free end is protonated,[18] thereby eliminating its coordinating tendency. For the ligand with the weaker coordinating ability, ethylene glycol, the monodentate form has greater relative stability, as would be expected. In the limit at unit activity of

---

[15] Other sets of values of Q_I and Q_{II} will fit the $\bar{n}$ data equally well or slightly better. The values of Q_{II} used here are, however, consistent with the values of k_2/k_{-2} obtained at lower temperatures and with the endothermic nature of reaction 2.

[16] S. W. Benson, *J. Amer. Chem. Soc.*, **80**, 5151 (1958).

[17] R. A. Clement and M. R. Rice, *ibid.*, **81**, 326 (1959).

[18] R. F. Childers, Jr., K. G. Vander Zyl, Jr., D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, **7**, 749 (1968).

water it comprises 77% of the sum of the monoglycol species.

Although the relatively large rate which is interpreted here to be associated with reaction 2 is larger than the rate for the aquation reactions of most chromium(III) complexes, the rate coefficient (k_{-2} = 4.8 × 10^{-3} sec^{-1} at 25°)[19] is not the largest observed for such reactions. Other relatively large rate coefficients for aquation of chromium(III) species are those for perchloratochromium(III) ion (7.6 × 10^{-3} sec^{-1} extrapolated to 25°)[20,21] and for trifluoromethylsulfonatochromium(III) ion (7.6 × 10^{-4} sec^{-1} at 25°).[21] Also pertinent for comparison to the present system is the large rate coefficient observed for conversion of the hydroxy–pentadentate EDTA chromium(III) complex to the corresponding tetradentate species (k = 4.8 × 10^{-3} sec^{-1} at 25°),[22] a transformation which involves the opening of a chelate ring. Since the reactant species in this reaction involves hydroxide ion coordinated to chromium(III), a substitution for water which is known to cause greater lability, one cannot be sure of the cause of the greater lability.

The stability of diglycolchromium(III) ion is much lower than expected on a statistical basis; this trend is observed also for the cobalt(III)–ethylenediamine system.[23] Three different diglycolchromium(III) species are possible even if isomers are not considered: $CrG_2(OH_2)_2^{3+}$, $CrG_2(OH_2)_3^{3+}$, and $CrG_2(OH_2)_4^{3+}$. From the values $Q_I = 0.35$ and $Q_{III} = 0.105$, one would estimate on a statistical basis: $Q_{22} \cong 0.022$, $Q_{21} \cong 0.23$, and $Q_{11} \cong 0.15$, in which the two subscripts denote the number of coordination sites occupied by each of the two coordinated glycol molecules. (The reactions forming a product with chelated glycol have the chelated monoglycol species as reactant.) With these values, one calculates that at $Z \cong 0.73$, the total concentration of species with two coordinated glycol molecules would be 41% of the total concentration of monoglycol species. The species in an equilibrated solution with this composition were separated by a column ion-exchange procedure; no diglycol species were detected, and correlations of spectral and $\bar{n}$ data in this composition of solvent do not need the presence of diglycolchromium(III) species. At the highest glycol concentrations studied, species with two or more coordinated glycol molecules would be predominant if the several equilibrium quotients were related by the appropriate statistical factor. The spectral data suggest the presence of such species at the highest Z values studied, but certainly not in the statistically expected amounts.

The difference in light absorption by the two glycolchromium(III) species with the species having the larger molar absorptivity being assigned the chelate structure is consistent with the interpretation of corresponding differences for other systems.[24] The unstable chelated glycolatochromium(III) ion formed as the initial product in the oxidation of chromium(II) by pentaammineglycolatocobalt(III) ion has a larger molar absorptivity than the final product, which is predominantly the monodentate species.[25] Chelated tetraaquoethylenediaminechromium(III) ion has a larger molar absorptivity than the corresponding protonated monodentate complex.[18] In the chelated forms of each of these complexes, the greater distortion from octahedral symmetry results in lower forbiddenness of the transitions.

[19] Statistical correction gives 2.4 × 10^{-3} sec^{-1}.

[20] K. M. Jones and J. Bjerrum, *Acta Chem. Scand.*, **19**, 974 (1965).

[21] A. Scott and H. Taube, *Inorg. Chem.*, **10**, 62 (1971).

[22] R. N. F. Thorneley, A. G. Sykes, and P. Gans, *J. Chem. Soc. A*, 1494 (1971).

[23] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

[24] R. E. Hamm, R. L. Johnson, R. H. Perkins, and R. E. Davis, *J. Amer. Chem. Soc.*, **80**, 4469 (1958).

[25] R. D. Butler and H. Taube, *ibid.*, **87**, 5597 (1965).

CONTRIBUTION NO. 4471 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY,
CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA 91109

Binding of Some Cyano- and Isocyanochromium(III) Complexes with Mercury(II), Silver(I), and Mercury Electrodes

BY STEVEN N. FRANK AND FRED C. ANSON

Received June 12, 1972

The reactions of $Cr(OH_2)_5CN^{2+}$, *cis*-$Cr(OH_2)_4(CN)_2^+$, and *fac*-$Cr(OH_2)_3(CN)_3$ with Hg^{2+} and Ag^+ to form binuclear and trinuclear adducts have been investigated. Equilibrium quotients evaluated include $[(CrNC)_2Hg^{6+}]/[CrCN^{2+}]^2[Hg^{2+}] = (1.3 \pm 0.6) \times 10^{15}$, $[(CrNC)_2Ag^{5+}]/[CrCN^{2+}]^2[Ag^+] = (5.6 \pm 5) \times 10^{10}$, $[CrNC^{2+}]/[CrCN^{2+}] = (4.8 \pm 1) \times 10^{-3}$, and $[CrNCH^{3+}]/[CrNC^{2+}][H^+] = 18 \pm 3$. Electrochemical reduction of the heavy-metal adducts was utilized to generate a variety of the unstable isocyanochromium(III) isomers at mercury electrodes. No adsorptive binding of any of these complexes to the surface of the mercury electrodes could be detected. Possible reasons for the contrasting behavior displayed by the (nonadsorbing) isocyanochromium(III) and (strongly adsorbing) isothiocyanatochromium(III) complexes are examined.

The recent work of Espenson and coworkers[1,2] describing the reaction of $Cr(OH_2)_5CN^{2+}$ with Hg^{2+} to form a stable binuclear adduct, $(H_2O)_5CrNCHg^{4+}$, attracted our interest because of the possibilities it suggested for substituting the positively charged surface of a mercury electrode for the Hg^{2+} ion to obtain the linkage-isomerized chromium(III) complex adsorbed on the electrode surface where its electrochemical behavior could be observed. The analogous system in which thiocyanate is the ligand by which

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

[2] J. H. Espenson and W. R. Bushey, *ibid.*, **10**, 2457 (1971).