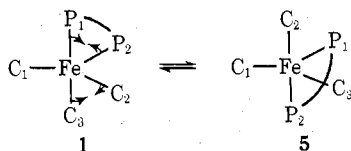phorus equatorial) but which still permits permutation of phosphorus environments and also carbonyl environments. For example, by holding the C_1–Fe bond fixed in space, structure 1 can be converted to structure 5 by bending the P_2–Fe–C_2 angle to 180° and decreasing

the P_1–Fe–C_3 angle to 120°. A rotation of 90° about the C_1–Fe bond gives structure 5.[5] This process equilibrates P_1 and P_2 and C_2 and C_3. If the process is repeated holding, this time, the C_2–Fe bond fixed in space, then C_1 and C_3 (as well as P_1 and P_2) will be equilibrated.

The proton nmr spectra of both the free and complexed ligand are complex (see Figures 1 and 2). This is undoubtedly due to the presence of short and long range coupling of the type described by Carty and Harris.[10,24,25] The type of spectrum obtained for Fe[$(CH_3)_2PCH_2CH_2P(CH_3)_2$](CO)$_3$ has been stated by King, *et al.*,[26] to be that expected for a $(CH_3)_2PCH_2$-$CH_2P(CH_3)_2$ complex with two magnetically equivalent phosphorus atoms; however, as already pointed out, the two phosphorus atoms cannot be magnetically equivalent.

Although the possibility of the previously reported

(24) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

(25) A. J. Carty and R. K. Harris, *Chem. Commun.*, 234 (1967).

(26) R. B. King, R. N. Kapoor, and L. W. Hauk, *J. Inorg. Nucl. Chem.*, **31**, 2179 (1969).

iron pentacarbonyl derivative *trans*-Fe[P(N(CH$_3$)$_2$)$_3$]$_2$-(CO)$_3$[10] having a stereochemically rigid structure at room temperature cannot be excluded, the mere absence of bands attributable to the cis isomer in the infrared spectrum does not preclude the possibility of a small, experimentally nonobservable amount of it being present. Even a small steady-state concentration of the cis isomer would be sufficient to permit intramolecular exchange. The temperature dependence of the proton spectra of $(CH_3)_2PCH_2CH_2P(CH_3)_2$ and Fe[$(CH_3)_2PCH_2CH_2P(CH_3)_2$](CO)$_3$ is, in part, somewhat similar to that of *trans*-Fe[P(N(CH$_3$)$_2$)$_3$]$_2$-(CO)$_3$.[10] Although the temperature dependence of the ^{1}H nmr spectrum of the above compound and of $(CH_3)_2$-PCH$_2$CH$_2$P(CH$_3$)$_2$ might be due, at least in part, to rotational restrictions at lower temperatures, the small changes involved in both cases could well be due to temperature-dependent solvent effects. In the case of Fe[$(CH_3)_2PCH_2CH_2P(CH_3)_2$](CO)$_3$ the somewhat larger temperature dependence is even more likely to be caused by temperature-dependent solvent effects since the reduction in freedom of motion of the complexed ligand will favor its interaction with the solvent.

Electrochemical Investigation of Tris(1,10-phenanthroline) Complexes of Chromium[1,2]

By DONALD M. SOIGNET*[3] AND LARRY G. HARGIS

Tris(1,10-phenanthroline)chromium(III) undergoes a one-electron reduction at -0.50 V *vs.* the sce followed by a series of reactions which converts all unreduced tris(1,10-phenanthroline)chromium(III) into diaquobis(1,10-phenanthroline)chromium(III). This conversion parallels that previously observed for the tris(2,2'-bipyridine)chromium(III) complex; however, the rate of conversion is slower and is both pH and temperature dependent. The diaquobis(1,10-phenanthroline)chromium(III) complex is reducible at the mercury electrode to the corresponding Cr(II) complex. In the presence of excess 1,10-phenanthroline the diaquobis(1,10-phenanthroline)chromium(II) reverts to the corresponding tris chromium(II) complex. In the absence of excess 1,10-phenanthroline, the diaquobis(1,10-phenanthroline)chromium(II) is converted to equimolar amounts of tris(1,10-phenanthroline)chromium(II) and tetraaquomono(1,10-phenanthroline)chromium(II).

Introduction

The tris(1,10-phenanthroline) complexes of Cr(III),

Cr(II), Cr(I), and Cr(0) have been prepared previously[4] and were found to be similar to the corresponding 2,2'-bipyridine complexes.[4,5] Information on the aqueous solution chemistry of these complexes is scarce and no studies of the electrochemical reduction behavior have been reported.

(4) S. Herzog and H. Aul, *Z. Naturforsch. B*, **15**, 617 (1960).

(5) S. Herzog, *Chem. Tech. (Berlin)*, **8**, 544 (1956).

The electrochemical behavior of the tris(2,2'-bipyridine)chromium(III) complex in aqueous solution has been established previously.[6-8] It was determined that the complex could be reduced at a mercury electrode to the corresponding Cr(II) complex which underwent a series of reactions in which any tris-(2,2'-bipyridine)chromium(III) remaining was converted to the diaquobis(2,2'-bipyridine)chromium(III). The following equations describe the reactions that occurred

$$[Cr(L)_3]^{3+} + 1e^- \longleftrightarrow [Cr(L)_3]^{2+} \quad E_{1/2} = -0.49 \text{ V} \quad (1)$$

$$[Cr(L)_3]^{2+} + 2H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Cr(L)_2(H_2O)_2]^{2+} + L \quad (2)$$

$$[Cr(L)_3]^{3+} + [Cr(L)_2(H_2O)_2]^{2+} \longrightarrow$$
$$[Cr(L)_3]^{2+} + [Cr(L)_2(H_2O)_2]^{3+} \quad (3)$$

$$[Cr(L)_2(H_2O)_2]^{3+} + 1e^- \longleftrightarrow$$
$$[Cr(L)_2(H_2O)_2]^{2+} \quad E_{1/2} = -0.72 \text{ V} \quad (4)$$
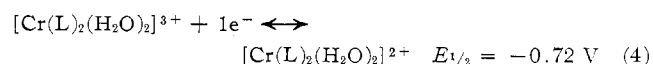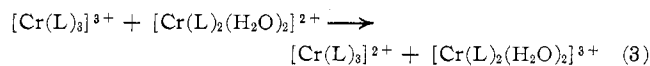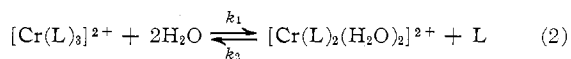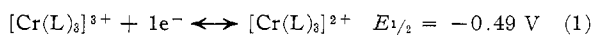
When "L" represents 2,2'-bipyridine, the equilibrium of eq 2 favors the existence of $[Cr(L)_3]^{2+}$; however, in a solution containing an excess of unreduced $[Cr(L)_3]^{3+}$, as occurs in a polarographic examination of $[Cr(L)_3]^{3+}$, the equilibrium is shifted away from the $[Cr(L)_3]^{2+}$ by the reaction depicted by eq 3. The symbol "$\longleftrightarrow$" represents a reversible polarographic reaction at the potential indicated.

Fischerová'[9] has investigated the behavior, at a mercury drop electrode, of the complex $[Cr(L)_3]^{3+}$ where "L" is the ethylenediamine molecule. He concluded that at pH 5–8, the complex underwent a one-electron reduction at the electrode to the corresponding tris(ethylenediamine)chromium(II) ion followed by a rapid ligand exchange in which all ethylenediamine was replaced by solvent. The result was the formation of the dichlorotetraaquochromium(II) ion. At a pH between 8 and 10.5 the tris(ethylenediamine)chromium(II) was found to be in equilibrium with diaquobis(ethylenediamine)chromium(II). The work of Pecsok and Bjerrum[10] indicates that this equilibrium favors the diaquo complex even when the solution contains a tenfold excess of free ethylenediamine.

A complete electrochemical investigation of tris-(1,10-phenanthroline)chromium(III) ion was initiated to determine whether its behavior would parallel that of the tris(2,2'-bipyridine)chromium(III) ion or that of the tris(ethylenediamine)chromium(III) ion. If it was found to parallel the bipyridine analog, the effect of the heavier, bulkier and more rigid 1,10-phenanthroline ligand on the value of k_1 and the equilibrium of eq 2 would also be investigated.

Experimental Section

Apparatus.—Electrochemical measurements were made with a Beckman Electroscan 30 equipped with a disk integrator. The integrator output was coupled to a modified Scallette pulse counter, Model SC-355.

The cell employed for the coulometric, polarographic, and cyclic voltametric studies consisted of a 100-ml water-jacketed beaker with a ground-glass neck. A platinum wire sealed through the bottom of the cell was connected to the mercury pool for the controlled-potential electrolysis. The dropping mercury,

sitting mercury drop, standard calomel, and auxiliary electrodes, along with the purge-gas inlet and outlet, were fitted ground-glass openings in the cover that in turn fitted onto the top of the cell. The open circuit m and t values of the capillary were 1.46 mg/sec and 3.5 sec in 0.1 M KCl at 25°. This gave a capillary constant of 1.59 $\text{mg}^{2/3}\text{sec}^{1/6}$.

Prepurified argon, used for deoxygenation and subsequent blanketing of the solution, was passed successively through solutions of vanadium(II) sulfate, chromium(II) chloride, and 0.1 M potassium chloride prior to passage through the sample. For the controlled-potential electrolysis experiments, after initial purging, the gas flow was discontinued and the cell sealed.

Absorption spectra were obtained with a Beckman DBG recording spectrophotometer.

Reagents.—All chemicals used were reagent grade. Unless otherwise stated, solution concentrations of the complexes were approximately 1 mM in a supporting electrolyte of 0.1 M potassium chloride. All solutions contained 0.1% Triton X-100 as a maximum suppressor.

A modification of the Burstall and Nyholm[11] procedure for the preparation of tris(2,2'-bipyridine)chromium(III) was used to prepare $[Cr(phen)_3](ClO_4)_3$. An acidic CrCl$_3$ solution was passed through a Jones (Zn amalgam) reductor into an oxygen-free solution of sodium acetate suspended above a sintered glass plate by constantly passing N$_2$ through the filter plate from the chamber beneath. The red suspension of chromous acetate formed on mixing was cooled by placing the entire system in an ice bath. With a positive, inert-atmosphere pressure, the solution was filtered through the sintered glass disk and the solid chromous acetate was collected on the filter. Water, previously purged of oxygen, was added to dissolve the chromous acetate. A solution containing 1,10-phenanthroline (>3 mol/mol of chromous acetate) in 0.23 M HClO$_4$ and sufficient deoxygenated methanol to ensure dissolution of the 1,10-phenanthroline was then added. The pH of the resulting black suspension was adjusted to a value between 1 and 2 and the suspension was oxidized by bubbling oxygen through the solution. Air can also be used, but the yield is reduced. The yellow crystals obtained after partial evaporation of the solvent were washed with CHCl$_3$ and recrystallized from hot water.

Anal. Calcd for $[Cr(C_{12}H_8N_2)_3](ClO_4)_3 \cdot 2H_2O$: C, 46.65; H, 3.02; N, 9.06. Found: C, 46.88; H, 2.75; N, 9.12.

Stability of Complexes.—Aqueous solutions of the tris(1,10-phenanthroline)chromium(III) ion in 0.1 M KCl at pH's ranging from 2 to 7 were prepared and examined daily over a period of several weeks. No change in uv or visible absorption or pH were noted throughout this period. Extraction of the stored solutions with chloroform indicated no free 1,10-phenanthroline had been produced in the aqueous solutions.

Procedures.—Absorption spectra of reduced solutions were obtained in a 1- or 10-mm glass-stoppered absorption cell fitted with a rubber septum to make it airtight. A portion of the reduced solution was transferred from the electrolysis vessel directly to the absorption cell. The cell was then emptied and refilled, all under pressure of argon gas. This process protected against the presence of oxygen and ensured that the recorded spectrum was that of the reduced material.

Kinetic data on the dissociation of $[Cr(phen)_3]^{2+}$ were obtained from the anodic and cathodic peak currents of cyclic voltammograms as described by Nicholson and Shain.[12] The anodic and cathodic currents used to obtain the rate constant were calculated from the anodic and cathodic peak currents and the current at the switching potential as described by Nicholson.[13]

All potentials were measured *vs.* sce unless otherwise stated.

Discussion

It has been shown that buffer components such as citrate and phosphate can participate in catalytic electron-exchange reactions with chromium(II) to form chromium(III) complexes[14] and that the polarographic behavior of tris(2,2'-bipyridine)chromium(III) differs in different buffers;[7] therefore all solutions used in this investigation were unbuffered. Solutions were adjusted to the desired pH values with HCl or NaOH.

(6) B. R. Baker and B. Dev Mehta, *Inorg. Chem.*, **4**, 848 (1965).

(7) B. V. Tucker, J. M. Fitzgerald, L. G. Hargis, and L. B. Rogers, *J. Electroanal. Chem.*, **13**, 400 (1967).

(8) D. M. Soignet and L. G. Hargis, *Inorg. Chem.*, **11**, 2349 (1972).

(9) A. Fischerová, *Collect. Czech. Chem. Commun.*, **30**, 1771 (1965).

(10) R. L. Pecsok and J. Bjerrum, *Acta Chem. Scand.*, **11**, 1419 (1957).

(11) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

(12) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

(13) R. S. Nicholson, *ibid.*, **38**, 1406 (1966).

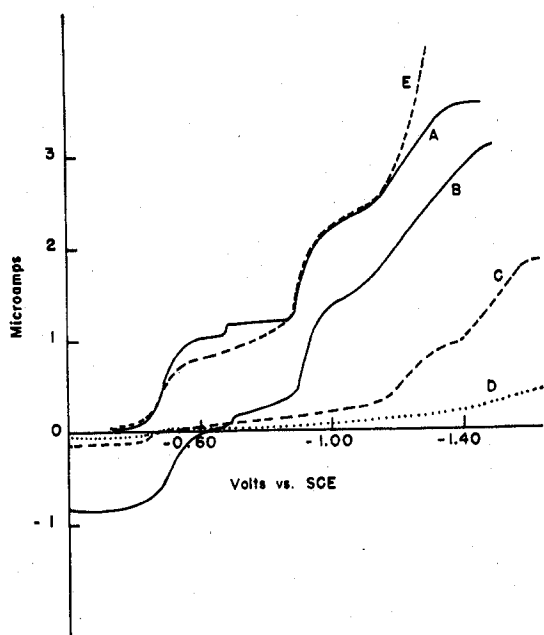(14) S. Herzog, *J. Inorg. Nucl. Chem.*, **8**, 557 (1958).

Figure 1.—Polarograms of 4.7×10^{-4} M [Cr(phen)$_3$]$^{3+}$ and of products of successive coulometric reductions in 0.1 M potassium chloride at pH 4.5 and 26°: (A) unreduced complex, (B) complex reduced 1 electron/molecule at -0.80 V ($n = 1$), (C) complex reduced a second electron/molecule at -1.00 V ($n = 2$); (D) complex reduced a third electron/molecule at -1.30 V ($n = 3$), and (E) complex reduced a total of 3 electrons/molecule and rapidly oxidized with oxygen gas.
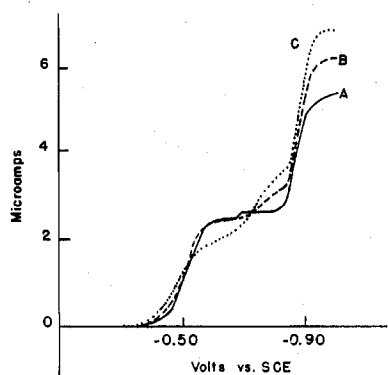

Figure 2.—Polarograms of 1.2×10^{-3} M [Cr(phen)$_3$]$^{3+}$ in 0.1 M potassium chloride at pH 4.4 at various temperatures: (A) 25°, (B) 37°, and (C) 43°.

Solution pH's were checked after various electrolyses to make certain that hydrogen consumption or evolution had not occurred and altered the acidity.

Tris(1,10-phenanthroline)chromium(III) Ion.—The electrochemical behavior of the tris(1,10-phenanthroline)chromium(III) ion, [Cr(phen)$_3$]$^{3+}$, in aqueous solution has not been previously reported. A typical polarogram of this complex in aqueous solution is shown in Figure 1. Three waves of approximately the same height were observed with $E_{1/2}$ of -0.50, -0.92, and -1.25 V, respectively. In addition, a smaller wave with $E_{1/2}$ of -0.70 V was also observed. The diffusion current constant, I, for the wave at -0.50 V, which is attributed to the one-electron reduction of [Cr(phen)$_3$]$^{3+}$ to [Cr(phen)$_3$]$^{2+}$, was calculated to have a value of 1.24 μA mmol^{-1} l. mg$^{-2/3}$ sec$^{-1/6}$ at 26° and pH 5. This value was relatively constant over the pH range of 1.5–7.0. At pH 4.5, the diffusion current

of the wave at -0.50 V was constant between 22 and 32°; however, it did decrease when the temperature was lowered to 1°. As the temperature was increased above 32°, there was a decrease in the diffusion current of the wave at -0.50 V and a corresponding increase in the diffusion current of the wave at -0.70 V. Polarograms obtained at the various temperatures are shown in Figure 2. Similar behavior had been observed previously[6,8] in the study of the tris(2,2'-bipyridine)-chromium(III) complex. In that system the changes were attributed to the transformation of tris Cr(III) complex to the diaquobis(2,2'-bipyridine)chromium-(III) complex according to eq 1–4. The similarity in polarographic behavior observed for [Cr(phen)$_3$]$^{3+}$ and [Cr(bipy)$_3$]$^{3+}$ led to the assumption that the [Cr(phen)$_3$]$^{3+}$ complex underwent similar changes. However, higher temperatures were necessary in the [Cr(phen)$_3$]$^{3+}$ to produce these changes suggesting that either the value of the rate constant, k_1, or of the equilibrium constant for eq 2 was less for the [Cr-(phen)$_3$]$^{3+}$ system than for the [Cr(bipy)$_3$]$^{3+}$ system.

In an effort to further characterize these initial processes cyclic voltammetric studies of the system were performed between -0.20 and -0.65 V. At a scan rate of 0.1 V/sec, a single cathodic wave with peak potential of -0.60 V and a single anodic wave with peak potential of -0.42 V were observed. Properties such as the ratio of peak currents and the shift of peak potential with change in scan rate (see ref 8 for detailed discussion) were all indicative of a reversible electrochemical reaction followed by an irreversible chemical reaction.[12] An examination of the proposed ligand-exchange reaction involving the [Cr(phen)$_3$]$^{2+}$ and water (eq 2, where L is 1,10-phenanthroline) indicates that in the presence of unreacted [Cr(phen)$_3$]$^{3+}$ eq 2 will appear to be an irreversible chemical reaction. The degree of irreversibility will be dependent on the position of the equilibrium and dependent on the velocity of the electron-exchange reaction (eq 3). For the complex system where L is 2,2'-bipyridine, reaction 3 was found to be irreversible and fast.[6] The [Cr-(bipy)$_2$(H$_2$O)$_2$]$^{2+}$ ion exists in the ground state in a low-spin configuration,[15] and since the [Cr(phen)$_2$(H$_2$O)$_2$]$^{2+}$ ion should also have a low-spin ground state, it is reasonable to expect reaction 3 to be irreversible and fast when L is 1,10-phenanthroline.

Table I shows typical cyclic voltammetric data obtained from a solution of [Cr(phen)$_3$]$^{3+}$ at pH 4.4 and varying temperatures. Utilizing the measured current values, the ratio of anodic to cathodic current was calculated at various scan rates and temperatures. These values in turn were compared to Nicholson's[13] tabulated values of the ratio of anodic to cathodic peak currents vs. the k_f value (where k_f is the rate constant of the irreversible chemical reaction and the elapsed time between the potential at which the scan is reversed and the $E_{1/2}$ of the cathodic wave) and values of k_1 for eq 2 were calculated for the various temperatures. These rate constants are smaller than those reported for the [Cr(bipy)$_3$]$^{3+}$ system.[8] An Arrhenius plot of this data was prepared. The least-squares line through the points had a correlation coefficient of -0.99. From the slope, an activation energy of 23.9 $\pm$

(15) J. M. Cambtree, D. W. Marsh, J. C. Tomkins, R. J. P. Williams, and W. C. Fernelius, *Proc. Chem. Soc., London*, 336 (1961).

TABLE I

CYCLIC VOLTAMMETRIC DATA FOR 4.9×10^{-5} M $[Cr(phen)_3]^{3+}$ [a]

Scan rate, V/sec	Temp, °C	Current, μA			Potential, V		k_f, sec^{-1}
		$(i_{cp})_0$	$(i_{ap})_0$	$(i_{sp})_0$	$(E_p)_c$	E_η	
0.02	22	12.1	7.2	6.1	−0.56	−0.70	0.009
0.01	22	8.6	4.3	3.9	−0.54	−0.69	0.010
0.004	22	5.0	2.1	2.0	−0.53	−0.64	0.008
0.02	25	12.6	6.6	5.8	−0.56	−0.70	0.017
0.01	25	8.5	3.9	3.2	−0.54	−0.68	0.016
0.004	25	4.5	1.5	1.9	−0.53	−0.63	0.012
0.04	30	18.7	10.5	9.4	−0.58	−0.71	0.025
0.02	30	12.3	6.2	4.7	−0.56	−0.68	0.026
0.02	31	12.2	6.0	4.6	−0.56	−0.68	0.029
0.01	31	7.6	2.8	3.1	−0.54	−0.63	0.030
0.02	32	18.2	9.6	8.5	−0.57	−0.69	0.036
0.01	32	11.9	5.2	4.6	−0.56	−0.68	0.036
0.10	37	31.1	16.5	17.6	−0.56	−0.67	0.068
0.02	37	11.2	3.7	4.1	−0.54	−0.65	0.068
0.20	39	47.4	25.9	29.8	−0.64	−0.75	0.081
0.10	39	31.4	16.0	18.7	−0.60	−0.67	0.088
0.04	43	14.9	5.0	5.8	−0.54	−0.63	0.143

[a] Solution of $[Cr(phen)_3]^{3+}$ in 0.1 M KCl at pH 4.4.

0.5 kcal/mol was calculated. A value of 20.3 kcal/mol was similarly obtained for $[Cr(bipy)_3]^{2+}$.[8]

The kinetic data accumulated from the preceding cyclic voltammetric experiments indicated that $[Cr(phen)_3]^{3+}$ could be only partially reduced at −0.60 V. Since the extent of reduction of the tris complex at −0.60 V was limited due to a catalytic dissociation to a free phenanthroline ligand, extent of reduction would be expected to increase as the temperature decreased. To test this hypothesis the results of reductions at a stirred Hg pool at −0.60 V at 26 and 1° were compared.

A solution of $[Cr(phen)_3]^{3+}$ at 26° could be reduced only 0.06 electron/molecule at −0.60 V. The polarogram of the resulting solution (Figure 3) did not show the wave originally present at −0.50 V for $[Cr(phen)_3]^{3+}$, but did contain a new wave with $E_{1/2}$ of −0.74 V. In addition, the polarogram became somewhat drawn out in the potential region of −0.80 to −1.20 V, making identification of the waves at −0.92 and −1.25 V more difficult. After this partial reduction the solution had become light orange and the uv spectrum of a chloroform extract of the solution indicated that 1 mol of phenanthroline per mole of original $[Cr(phen)_3]^{3+}$ was free in solution. A polarogram of the solution remaining after the extraction is also shown in Figure 3. Three distinct waves with values of −0.74, −0.92, and −1.25 V are observed. Every experimental result paralleled that observed for the corresponding bipyridine system which leads us to conclude that the solution remaining after chloroform extraction contained $[Cr(phen)_2(H_2O)_2]^{3+}$. The uv spectrum of the aqueous portion after extraction shown in Figure 5B resembled the uv spectrum of $[Cr(phen)_2(H_2O)_2]^{3+}$ as reported by Phillips.[16] The preceding data support the assumption that the complex resulting from the decomposition of the $[Cr(phen)_3]^{3+}$ was indeed the diaquo complex.

At a lower temperature, such as 1°, the rate constant, k_1, for eq 2 should be smaller. This reduced rate should have two effects: it should allow a larger amount of the tris complex to be reduced at −0.60 V, and it may allow production of enough $[Cr(phen)_3]^{2+}$ to be observed polarographically and spectrophotometrically. On reduction at −0.60 V at 1° a total of 0.5 electron/molecule was added before the current stopped

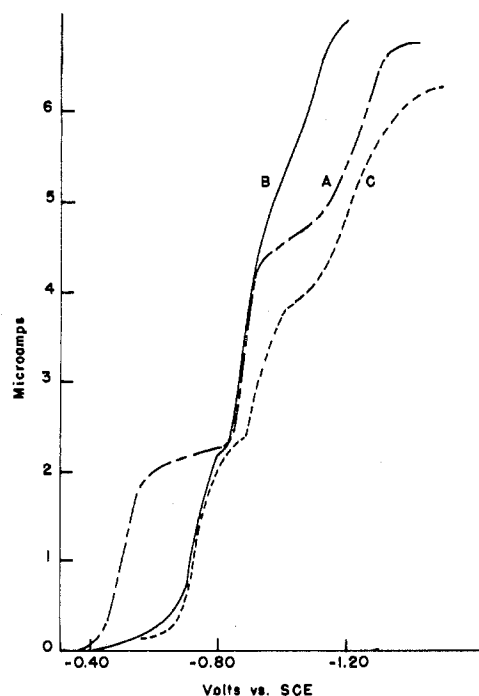(16) M. G. Phillips, Ph.D. Thesis, Syracuse University, Syracuse, N. Y., 1966.

Figure 3.—Polarograms of 9.6×10^{-4} M $[Cr(phen)_3]^{3+}$ in 0.1 M potassium chloride at 26° and pH 4.1: (A) unreduced complex, (B) complex reduced 0.06 electron/molecule at −0.6 V, and (C) reduced complex ($n = 0.06$) remaining after chloroform extraction.
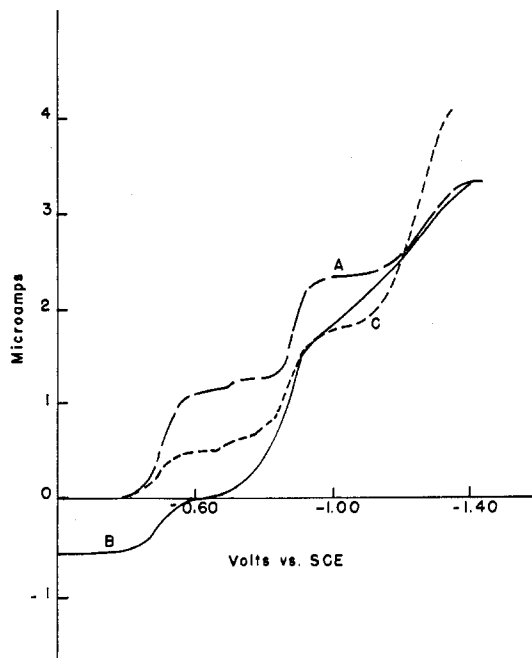

Figure 4.—Polarograms of 7.2×10^{-4} M $[Cr(phen)_3]^{3+}$ in 0.1 M potassium chloride at pH 5.2 and 1°: (A) unreduced complex, (B) complex reduced 0.50 electron/molecule at −0.60 V, and (C) reduced complex rapidly oxidized with oxygen gas.

flowing. The solution was green-yellow with visible absorption maxima at 727 and 483 nm and a shoulder at 540 nm. The polarogram of this solution, shown in Figure 4 contained an anodic wave with $E_{1/2}$ of −0.50 V whose diffusion current was approximately half that of the original cathodic wave at −0.50 V. The anodic wave and the visible absorption spectrum were apparently characteristic of $[Cr(phen)_3]^{2+}$.

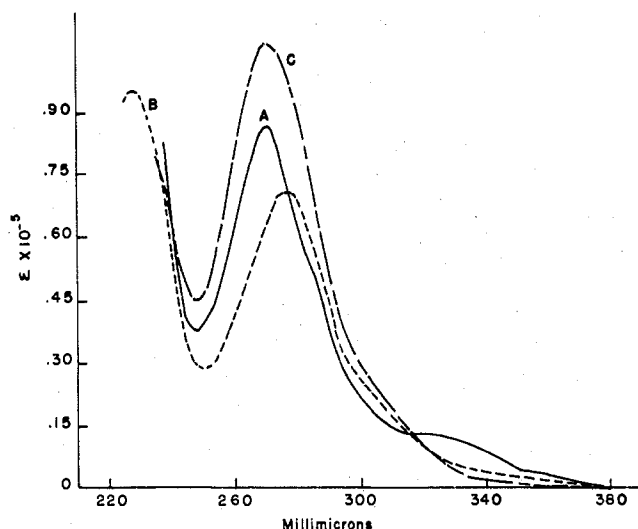Figure 5.—Ultraviolet spectra of complexes in 0.1 M potassium chloride solution: (A) (Cr(phen)₃]³⁺, (B) [Cr(phen)₂(H₂O)₂]³⁺, prepared *in situ* from [Cr(phen)₃]³⁺, and (C) [Cr(phen)₃]²⁺.

When the solution resulting from the 0.5 electron/ molecule reduction of the [Cr(phen)₃]³⁺ was transferred under argon pressure into 1 ml of 0.1 M KCl saturated with oxygen gas and through which oxygen gas was bubbling, it immediately became yellow. Extraction with chloroform indicated that the solution contained 1 mol of free 1,10-phenanthroline per 2 mol of original tris Cr(III) complex. The polarogram of the aqueous solution before extraction is shown in Figure 4C. It contains a cathodic wave at −0.50 V with diffusion current approximately the same as that of the original anodic wave observed for the reduced solution. Results obtained from polarographic, cyclic voltammetric, and controlled-potential electrolysis examination of the oxidized solution between −0.20 and −0.60 V were identical with those obtained for a solution of [Cr(phen)₃]³⁺. Therefore, it can be concluded that [Cr(phen)₃]²⁺ can be characterized by an anodic wave with $E_{1/2}$ of −0.50 V, a green-yellow color and absorption maxima at 727 and 483 nm and a shoulder at 540 nm. Herzog[4] has reported [Cr(phen)₃]²⁺ to be an olive color. Oxidation of the [Cr(phen)₃]²⁺ by oxygen in an environment void of large quantities of the reduced material proceeds to the formation of [Cr(phen)₃]³⁺.

To investigate further the reduced states of [Cr(phen)₃]³⁺, a solution of [Cr(phen)₃]³⁺ was reduced at −0.80 V which proceeded until a total of 1 electron/ molecule had been added. The reduction required approximately 0.5 hr. The solution at this time was green-yellow with a spectrum containing maxima at 727 and 483 nm and a shoulder at 540 nm. The polarogram of the reduced solution shown in Figure 1 contained an anodic wave at −0.50 V. The diffusion current of this wave was approximately equal that of the original cathodic wave with the same $E_{1/2}$. The solution's visible spectrum and polarographic behavior indicated that the major species present following the one-electron reduction was [Cr(phen)₃]²⁺. Assuming that all of the original [Cr(phen)₃]³⁺ was reduced to the [Cr(phen)₃]²⁺ by the procedure described above, the diffusion current of the anodic wave at −0.50 V
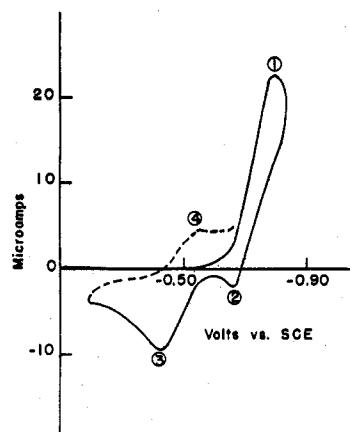

Figure 6.—Cyclic voltammogram of a 5.4 × 10⁻⁴ M solution of [Cr(phen)₂(H₂O)₂]³⁺ and 1,10-phenanthroline at 26° and pH 5.0. Scan rate was 0.1 V/sec.

was used to calculate a diffusion current constant of 1.29 for [Cr(phen)₃]²⁺. The uv spectrum of the [Cr(phen)₃]²⁺ shown in Figure 5C was similar to that of the original [Cr(phen)₃]³⁺ with the exception that it contained no shoulder at 330 nm and that its molar absorptivity at the λ_{max} was larger than that for the 3+ complex.

The results of further successive reductions at more cathodic potentials closely paralleled those of the corresponding bipyridine system.[8] The resulting polarograms are shown in Figure 1. Insoluble green Cr(I) and black Cr(0) complexes were produced similar to those reported by Herzog.[4,5] Rapid oxidation of the black Cr(0) product produced [Cr(phen)₃]³⁺ which was characterized in the same manner as [Cr(bipy)₃]³⁺ formed by oxidation of a similar Cr(0)–bipy complex.[8]

Diaquobis(1,10-phenanthroline)chromium(III)   Ion with 1,10-Phenanthroline.—From the data it is evident that attempts to reduce [Cr(phen)₃]³⁺ at room temperature and a stirred mercury pool resulted in conversion of the [Cr(phen)₃]³⁺ to the [Cr(phen)₂(H₂O)₂]³⁺ ion and free 1,10-phenanthroline. The rate constant for the ligand exchange reaction, k_1, has been measured at various temperatures, but the equilibrium of eq 2 in the absence of external forces has not been established. This is most easily accomplished by reduction of [Cr(phen)₂(H₂O)₂]³⁺ in the presence of 1,10-phenanthroline. If the equilibrium constant for eq 2 is small (L = 1,10-phenanthroline) as was observed in the case when L was 2,2′-bipyridine, then the product remaining after reduction would be [Cr(phen)₃]²⁺. A cyclic voltammogram of the bis complex with free 1,10-phenanthroline obtained by scanning between −0.20 and −0.80 V is shown in Figure 6. The first scan (solid line) produced a cathodic wave with E_p of −0.75 V (1), and two anodic waves with E_p of −0.66 V (2) and −0.42 V (3), respectively. On the second scan (dashed line), a new cathodic wave with E_p of −0.55 V was observed in addition to the waves previously mentioned. The appearance of two anodic waves after reduction of the [Cr(phen)₂(H₂O)₂]³⁺ suggests that the initial reduction product [Cr(phen)₂(H₂O)₂]²⁺ underwent a chemical reaction producing a species that was oxidizable at −0.42 V. The cathodic wave at −0.55 V observed on the second and subsequent scans was due to the reduction of the species

previously oxidized at −0.42 V. Both waves 3 and 4 persisted at slow scan rates (0.004 V/sec) and were in the potential range where waves had been observed previously for a solution of [Cr(phen)₃]³⁺, leading to the assumption that the product of the chemical reaction involving [Cr(phen)₂(H₂O)₂]²⁺ was indeed [Cr-(phen)₃]²⁺.

Since we had earlier characterized the polarographic and spectral properties of [Cr(phen)₃]²⁺, a controlled-potential electrolysis was performed at −0.80 V with the intention of comparing the properties of the reduced solution to those of [Cr(phen)₃]²⁺. The reduction proceeded for an equivalent of 1 electron/molecule. The solution at the time was green-yellow. Its visible spectrum contained maxima at 727 and 483 nm and a shoulder at 540 nm and the uv spectrum was identical with that of [Cr(phen)₃]²⁺ shown in Figure 5C. The polarogram of the reduced solution contained only one anodic wave at −0.50 V. These properties are all characteristic of a solution of [Cr(phen)₃]²⁺. Measurements of the uv absorbance and the diffusion current of the anodic wave at −0.50 V showed that the concentration of [Cr(phen)₃]²⁺ was equal to that of the original [Cr(phen)₂(H₂O)₂]³⁺. Oxidation of the reduced solution with oxygen as described earlier resulted in a solution whose spectral and electrochemical properties were identical with those previously observed for a solution of [Cr(phen)₃]³⁺, again indicating that the product of the reduction of [Cr(phen)₂-(H₂O)₂]³⁺ in the presence of 1,10-phenanthroline is [Cr(phen)₃]²⁺. These experiments clearly show that the equilibrium of eq 2 is in favor of the [Cr(phen)₃]²⁺.

Diaquobis(1,10-phenanthroline)chromium(III) Ion. —The diaquobis (1,10-phenanthroline)chromium(III) was prepared *in situ* from the [Cr(phen)₃]³⁺ complex. Catalytic amounts of [Cr(phen)₃]²⁺ were produced by reducing small quantities of [Cr(phen)₃]³⁺ at the stirred mercury pool which, in turn, converted all remaining [Cr(phen)₃]³⁺ to [Cr(phen)₂(H₂O)₂]³⁺ and 1,10-phenanthroline. The free 1,10-phenanthroline was removed by chloroform extraction and the solution remaining contained only the [Cr(phen)₂(H₂O)₂]³⁺ complex. It was this solution whose electrochemical properties were investigated. As stated earlier, the uv spectrum of this solution and that reported for a solution of [Cr(phen)₂(H₂O)₂]³⁺ prepared from the solid [Cr(phen)₂(H₂O)₂]³⁺ were identical.

The polarogram of the diaquo complex is shown in Figure 7. Two waves with $E_{1/2}$ of −0.74 and −0.85 V, respectively, are easily discernible. At pH 4 and 26°, the wave at −0.74 V had a diffusion current constant of 1.32. Between pH 2 and 3.4, the value increased to 1.50. Above pH 5 all waves merged.

A cyclic voltammogram of the solution was similar to that obtained for a solution of the [Cr(phen)₂-(H₂O)₂]³⁺ in the presence of phenanthroline (*i.e.*, a single cathodic wave at −0.80 V and two anodic waves at −0.66 and −0.42 V on the first sweep and an additional cathodic wave at −0.52 V on the next and subsequent scans). The new anodic and cathodic waves appeared at the same potential as did waves observed for a solution of [Cr(phen)₃]³⁺.

A solution of the diaquo complex was reduced at a stirred mercury pool at −0.80 V and an amount of current equivalent to 1 electron/molecule could be
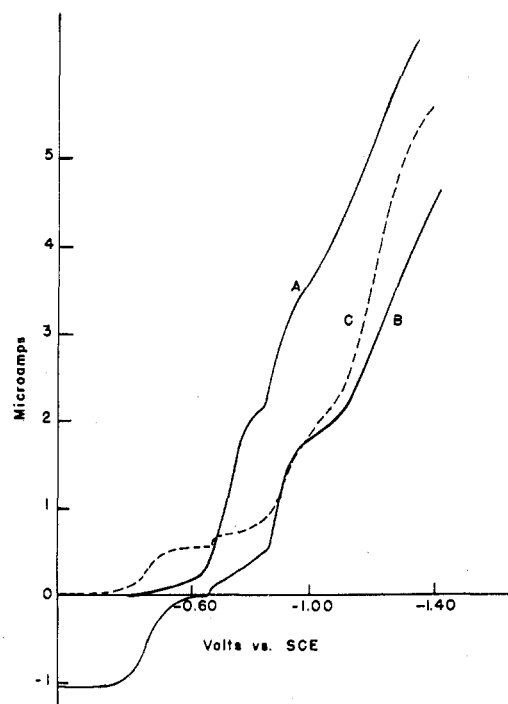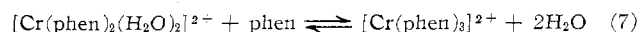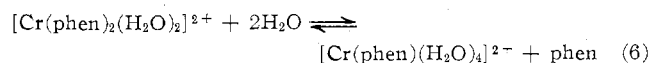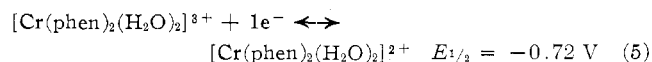

Figure 7.—Polarograms of 9.6 × 10⁻⁴ *M* [Cr(phen)₂(H₂O)₂]³⁺ in 0.1 *M* potassium chloride at 26° and pH 4: (A) unreduced complex, (B) complex reduced 1 electron/molecule at −0.80 V, and (C) complex reduced 1 electron/molecule and rapidly oxidized with oxygen gas.

passed. The solution became green-yellow and had a visible absorption spectrum containing maxima at 727 and 483 and a shoulder at 540 nm. The polarogram of the reduced solution possessed an anodic wave at −0.50 V. Using the previously calculated diffusion current constant for [Cr(phen)₃]²⁺ and assuming that this wave was the result of [Cr(phen)₃]²⁺ in solution, its concentration was determined to be half that of the original diaquobis(1,10-phenanthroline)chromium(III) complex. To verify that [Cr(phen)₃]²⁺ was indeed the material in solution responsible for the anodic wave at −0.50 V, the solution was oxidized rapidly with oxygen gas. The solution immediately became yellow and the results of electrochemical investigation between 0 and −0.60 V were identical with those recorded for a solution of [Cr(phen)₃]³⁺. The polarogram of the oxidized solution is shown in Figure 7. Since 1,10-phenanthroline was not originally present in the solution of the diaquobis(1,10-phenanthroline)chromium(III), the [Cr(phen)₃]²⁺ resulting from the reduction of the [Cr(phen)₂(H₂O)₂]³⁺ must be formed by a ligand exchange between two molecules of the bis complex forming a tris and a mono complex. A suggested reaction mechanism is shown below.

[Cr(phen)₂(H₂O)₂]³⁺ + 1e⁻ ⇌

[Cr(phen)₂(H₂O)₂]²⁺ $E_{1/2}$ = −0.72 V   (5)

[Cr(phen)₂(H₂O)₂]²⁺ + 2H₂O ⇌

[Cr(phen)(H₂O)₄]²⁺ + phen   (6)

[Cr(phen)₂(H₂O)₂]²⁺ + phen ⇌ [Cr(phen)₃]²⁺ + 2H₂O   (7)

Summary

The tris(1,10-phenanthroline)chromium(III) complex like the tris(2,2′-bipyridine)chromium(III) com-

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.

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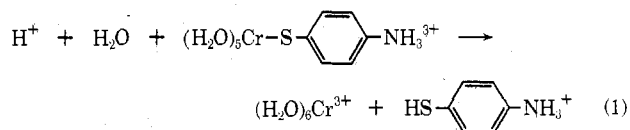
BY LEON E. ASHER AND EDWARD DEUTSCH*

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 $-d[\ln (\mathrm{CrSR^{3+}})]/dt = k_0 + k_1(\mathrm{H^+})$. 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 $-d[\ln (\mathrm{CrSR^{3+}})]/dt = k(\mathrm{oxidant})$. 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 ·SR$^+$, but not molecular oxygen, are effective oxidants.

Introduction

The chemistry of $(\mathrm{H_2O})_5\mathrm{CrX}^{n+}$ 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 $(\mathrm{H_2O})_5\mathrm{CrSR}^{n+}$ 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 $(\mathrm{H_2O})_5\mathrm{CrSR}^{n+}$ 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

$$\mathrm{H^+} + \mathrm{H_2O} + (\mathrm{H_2O})_5\mathrm{Cr\text{-}S}\!\!-\!\!\left\langle\bigcirc\right\rangle\!\!-\!\!\mathrm{NH_3^{3+}} \longrightarrow$$

$$(\mathrm{H_2O})_6\mathrm{Cr^{3+}} + \mathrm{HS}\!\!-\!\!\left\langle\bigcirc\right\rangle\!\!-\!\!\mathrm{NH_3^+} \quad (1)$$

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.