the $x^2 - y^2$ orbital would be lowered and a lower energy transition would be expected and is found, Table VI.

**The $[Zn(dacoda)(H_2O)] \cdot 2H_2O$ Complex.**—This complex is isomorphous with the corresponding Ni(II) complex as evidenced by the powder pattern, Table V, and there is little doubt that this structure is maintained in solution.

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# Electrochemical Investigation of Tris(2,2'-bipyridine) Complexes of Chromium(III)

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Tris(2,2'-bipyridine)chromium(III) undergoes a one-electron reduction at −0.50 V followed by a series of reactions which converts all unreduced tris(2,2'-bipyridine)chromium(III) to diaquobis(2,2'-bipyridine)chromium(III) and free 2,2'-bipyridine. The diaquobis(2,2'-bipyridine)chromium(III) complex can be reduced to the corresponding chromium(II) complex. In the presence of excess 2,2'-bipyridine, the diaquobis(2,2'-bipyridine)chromium(II) forms the tris(2,2'-bipyridine)chromium(II) complex by ligand exchange. In the absence of excess 2,2'-bipyridine, the final products are equimolar quantities of the tris(2,2'-bipyridine)chromium(II) and the tetraaquo(2,2'-bipyridine)chromium(II) complexes.

## Introduction

The tris(2,2'-bipyridine)chromium(III) ion has been the subject of several electrochemical studies. In aprotic solvents, such as acetonitrile, the tris complex apparently reduces in four well-defined, one-electron steps to the $[Cr(bipy)_3]^-$ anion.[3] The electrochemistry of this ion in water, however, is not simple or well understood and there is still considerable lack of agreement among investigators of this system.

Using a commutator technique to obtain current-voltage curves, Vlcek[4] reported three polarographic waves ($E_{1/2}$ *vs.* sce of −0.36, −0.73, and −1.38 V) for the tris(2,2'-bipyridine)chromium(III) ion in aqueous 0.5 *M* sodium chloride supporting electrolyte. By comparison of the wave heights with those for the hexaamminechromium(III) ion, Vlcek concluded that each of the waves corresponded to a reversible one-electron transfer, resulting finally in a tris(2,2'-bipyridine)chromium(0) complex. Vlcek reported no evidence of dissociation of the complex during any stage of the reduction.

Using conventional polarographic techniques Baker and Dev Mehta[5] and Tucker, *et al.*,[6] obtained four polarographic waves with half-wave potentials that were substantially different from those obtained by Vlcek. From the behavior of the first two polarographic waves with regard to temperature and pH, Baker and Dev Mehta[5] suggested the mechanism shown below whereby the $[Cr(bipy)_3]^{3+}$ underwent catalytic ligand exchange at the dme surface to $[Cr(bipy)_2(H_2O)_2]^{3+}$ which reduced more cathodically than the tris complex.

In the following equations the symbol $\rightleftarrows$ represents polarographically reversible reaction at the half-wave potential indicated

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

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

$$[Cr(bipy)_3]^{3+} + [Cr(bipy)_2(H_2O)_2]^{2+} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [Cr(bipy)_3]^{2+} + [Cr(bipy)_2(H_2O)_2]^{3+} \quad (3)$$

$$[Cr(bipy)_2(H_2O)_2]^{3+} + e^- \rightleftarrows [Cr(bipy)_2(H_2O)_2]^{2+} \quad E_{1/2} = -0.72\text{ V} \quad (4)$$

Although Baker and Dev Mehta did investigate the reduction of $[Cr(bipy)_3]^{3+}$, they did not report on the further reduction of the resulting chromium(II) species. This paper presents a detailed study of the entire system, namely, $[Cr(bipy)_3]^{3+}$, $[Cr(bipy)_2(H_2O)_2]^{3+}$ + bipyridine, and $[Cr(bipy)_2(H_2O)_2]^{3+}$, using polarographic, controlled-potential electrolysis, and cyclic voltammetric techniques. Cyclic voltammetry is particularly well suited to studying chemical reactions following an electron transfer[7,8] and we found it very useful in helping to characterize the systems studied here. In addition, several interesting observations are

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[3] Y. Sato and N. Tanaka, *Bull. Chem. Soc. Jap.*, **42**, 1021 (1969).

[4] A. A. Vlcek, *Nature (London)*, **189**, 393 (1961).

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

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

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

[8] R. S. Nicholson and I. Shain, *ibid.*, **38**, 1406 (1966).

noted concerning various techniques used to oxidize the reduced complexes.

## 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 voltammetric 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 into ground-glass openings in the cover which 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 the 0.1 *M* KCl at 25° yielding a capillary constant of 1.59 $mg^{2/3}$ $sec^{1/6}$.

Prepurified argon, employed to deoxygenate and subsequently blanket 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 was sealed.

Absorption spectra were obtained with a Beckman DBG recording spectrophotometer.

**Reagents.**—All chemicals used were reagent grade. Unless otherwise stated, concentrations of the complexes were approximately 1 m*M* in a supporting electrolyte of 0.1 *M* potassium chloride. All solutions contained 0.01% Triton X-100 as a maximum suppressor.

A modification of the procedure of Burstall and Nyholm[9] was used to prepare $[Cr(bipy)_3](ClO_4)_3$. 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 chromium(II) 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 chromium(II) acetate. A solution containing 2,2′-bipyridine (>3 mol/mol of chromium(II) acetate) in 0.23 *M* $HClO_4$ and sufficient deoxygenated methanol to ensure dissolution of the bipyridine 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 $[Cr(C_{10}H_8N_2)_3](ClO_4)_3$: C, 44.01; H, 2.93; N, 10.26. Found: C, 43.78; H, 3.00; N, 10.50.

**Stability of Complexes.**—The ultraviolet absorption spectra of the tris- and bis(bipyridine) complexes of chromium(III) are slightly different from each other and, in addition, the presence of free bipyridine in a solution of the tris or bis complex can be observed spectrophotometrically. Aqueous solutions of the tris(2,2′-bipyridine)chromium(III) ion in 0.1 *M* KCl at pH ranging from 2 to 7 were prepared and examined daily over a period of several weeks. No change in the absorption spectra or pH were noted throughout this time. Extraction of the stored solutions with chloroform indicated no free bipyridine had been produced in the aqueous solutions.

**Procedures.**—Absorption spectra of reduced solutions were obtained in a 1- or 10-mm glass airtight-stoppered absorption cell fitted with a rubber septum. 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 $[Cr(bipy)_3]^{2+}$ were obtained from the anodic and cathodic peak currents of cyclic voltammograms as described by Nicholson and Shain. 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.[10] All potentials were measured *vs.* sce unless otherwise stated.

## Discussion

It has been reported that chromium bipyridine complexes are not stable in strongly acidic or basic solutions.[6] Since many common buffer components such as citrate and phosphate participate in catalytic electron-exchange reactions with chromium(II) to form chromium(III) complexes[11] and because polarographic behavior has been shown to differ in such buffers,[6] unbuffered solutions were used throughout this study. Solutions were adjusted to desired pH values by addition of HCl or NaOH.

**Tris(2,2′-bipyridine)chromium(III) Ion.**—Since previous reports on the polarographic behavior of this species are not in complete agreement, we felt it necessary to make our own polarographic study prior to the controlled-potential electrolysis and cyclic voltammetric experiments. Our data confirmed the polarographic results of Baker and Dev Mehta.[5]

In order better to characterize the behavior of $[Cr(bipy)_3](ClO_4)_3$, controlled-potential electrolyses were planned for a suitable potential on the limiting-diffusion current plateau of each polarographic wave. The reduced solutions were examined polarographically, cyclic voltammetrically, and spectrophotometrically. Figure 1 shows the polarograms of a solution of $[Cr(bipy)_3]^{3+}$ and of the products of successive coulometric reductions.

When a solution of the tris complex was electrolyzed at −0.65 V at a stirred mercury pool, only 0.06 electron/molecule could be added before current flow stopped. The solution color changed from bright yellow to orange and the ultraviolet spectrum showed the presence of free bipyridine in the solution. The free bipyridine was removed by a chloroform extraction, and the extract, after comparison with standards, was found to contain essentially 1 mol of bipyridine per mole of original complex. A similar observation was reported by Tucker, *et al.*[6] The polarogram of the aqueous solution that remained after chloroform extraction is shown in Figure 2. The cathodic wave at $E_{1/2}$ = 0.49 V was no longer present and a new wave of approximately equal height appeared at $E_{1/2} = -0.74$ V.

According to Baker's mechanism the new wave at $E_{1/2} = -0.74$ V is the result of a new species, $[Cr(bipy)_2(H_2O)_2]^{3+}$, formed by the process described by reactions 1–3; therefore, the presence of $[Cr(bipy)_3]^{2+}$ should be detected when solution conditions are adjusted to decrease the rate constant, $k_1$. This was most easily accomplished by lowering the solution temperature. A solution of $[Cr(bipy)_3]^{3+}$ was adjusted to pH 7 and the solution was cooled to about 1° by passing ice water through the cell jacket. The polarogram, shown in Figure 3, exhibited three waves of approximately equal heights. When this solution was electrolyzed at −0.60 V at a stirred mercury pool, approximately 0.3 electron/molecule was added before current stopped (compared with 0.06 electron/molecule at 26°). The solution was deep red, exhibiting absorption maxima at 472 and 562 nm. The polarogram of this solution, shown in Figure 3, contained an anodic wave at $E_{1/2}$ =

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

[10] R. S. Nicholson, *Anal. Chem.*, **37**, 1351 (1963).

[11] S. Herzog, *J. Inorg. Nucl. Chem.*, **8**, 557 (1958).

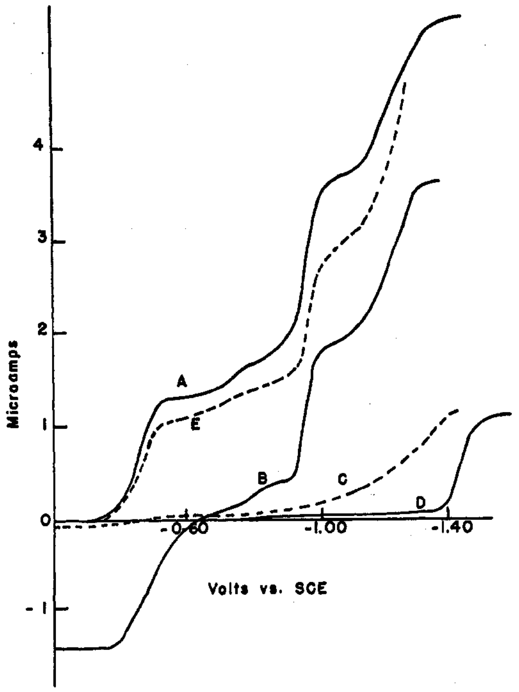

Figure 1.—Polarograms of 7.7 × $10^{-4}$ *M* $[Cr(bipy)_3]^{3+}$ and of products of successive coulometric reductions in 0.1 *M* potassium chloride at 26°, pH 7: (A) unreduced complex; (B) complex reduced 1 electron/molecule at −0.80 V (*n* = 1); (C) complex reduced a second electron/molecule at −1.00 V (*n* = 2); (D) complex reduced a third electron/molecule at −1.40 V (*n* = 3); (E) complex reduced a total of 3 electrons/molecule and rapidly oxidized with oxygen gas.

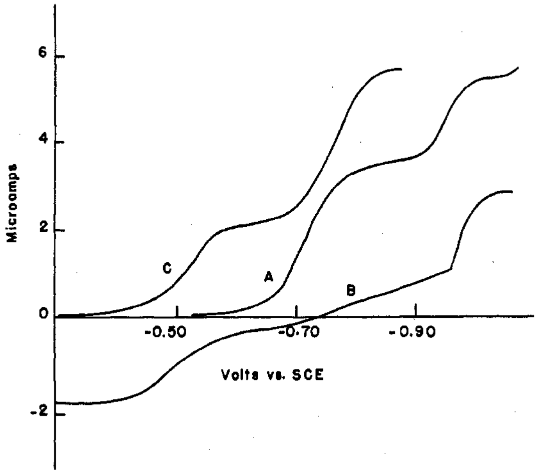

Figure 2.—Polarograms of 1.6 × $10^{-3}$ *M* $[Cr(bipy)_2(H_2O)_2]^{3+}$ in 0.1 *M* potassium chloride at 26° and pH 3.5: (A) unreduced complex; (B) complex reduced 1 electron/molecule at −0.80 V; (C) reduced solution oxidized rapidly with oxygen gas.

0.49 V whose height was approximately one-third the height of the original cathodic wave. The spectrum and the polarogram were characteristic of $[Cr(bipy)_3]^{2+}$. The cathodic wave attributed to $[Cr(bipy)_2(H_2O)_2]^{3+}$ was also present at $E_{1/2} = -0.77$ V. The polarogram taken before electrolysis exhibited a distinct wave at $E_{1/2} = -1.33$ V. After electrolysis, the wave in this region was somewhat larger and less distinct and shifted to $E_{1/2} = -1.20$ V. This shift and increase in size is attributed to the effects of free bipyridine in solution formed along with the $[Cr(bipy)_2(H_2O)_2]^{3+}$. On standing in the electrolysis cell, the solution lost its intense red color and its anodic polarographic wave, while at the same time, the wave at $E_{1/2} = -0.77$ V increased in amplitude. The anodic wave at $E_{1/2} = -0.49$ V and the absorption maxima at 472 and 562 nm are attributed to $[Cr(bipy)_3]^{2+}$.

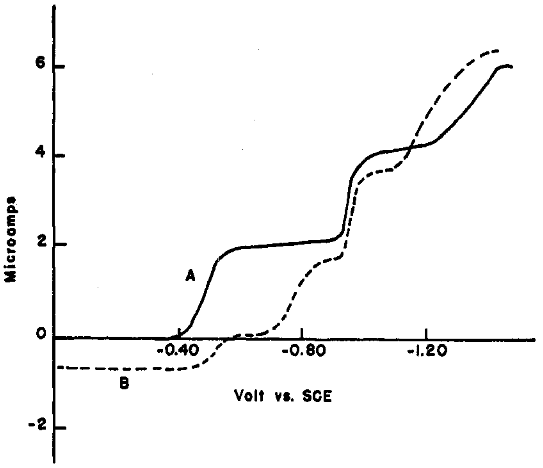

Figure 3.—Polarograms of 1.4 × $10^{-3}$ *M* $[Cr(bipy)_3]^{3+}$ in 0.1 *M* potassium chloride at 1° and pH 7: (A) unreduced complex; (B) complex reduced 0.27 electron/molecule at −0.60 V.

When a solution of the tris complex was electrolyzed at −0.80 V, a potential sufficiently cathodic to cause reduction of either $[Cr(bipy)_3]^{3+}$ or $[Cr(bipy)_2(H_2O)_2]^{3+}$, a total of about 1 electron/molecule could be passed before current stopped. The resulting solution was deep red and had visible absorption maxima at 472 and 562 nm and was similar to results reported by Baker[5] for a solution of $[Cr(bipy)_3]^{2+}$. The polarogram of this solution (Figure 1) showed an anodic wave at $E_{1/2} = -0.49$ V with the same limiting diffusion current as the first cathodic wave ($E_{1/2} = -0.49$ V) of the original $[Cr(bipy)_3]^{3+}$ complex. The visible absorption spectrum and the position of the anodic polarographic wave were the same as obtained from a solution of the tris complex reduced only 0.3 electron/molecule at 1° and were attributed to the species $[Cr(bipy)_3]^{2+}$. Assuming that all the original $[Cr(bipy)_3]^{3+}$ was converted to $[Cr(bipy)_3]^{2+}$, the diffusion current constant, *I*, for this chromium(II) species was calculated to be 1.16 $\mu$A m$M^{-1}$ mg$^{-2/3}$ sec$^{-1/6}$.

When a solution of the tris complex, previously reduced 1 electron/molecule at −0.80 V, was further reduced at −1.00 V, an additional 1 electron/molecule was passed before current flow stopped. The solution appeared blue but when a portion of the solution was transferred under argon to an oxygen-free container and centrifuged, a blue precipitate was separated leaving a colorless solution. Herzog has reported that $[Cr(bipy)_3]^{+}$ is blue.[11] A polarogram of the blue suspension expectedly showed very little electroactivity (Figure 1).

The blue suspension was subjected to electrolysis at −1.40 V. The electrolysis was slow requiring over 2 hr to pass an amount of current corresponding to 1.0 electron/molecule. A suspension of a black precipitate in a colorless solution was obtained. Herzog reported the $[Cr(bipy)_3]^{0}$ complex to be black.[11]

As expected, no polarographic activity was observed at potentials less cathodic than −1.4 V. Polarographic

TABLE I

CYCLIC VOLTAMMETRIC DATA FOR 5.5 × $10^{-5}$ *M* $[Cr(bipy)_3]^{3+}$ [a]

| Scan rate, V/sec | Temp, °C | Current, μA | | | Potential, V | | $k_f$, sec$^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | $(i_{cp})_0$[b] | $(i_{ap})_0$[b] | $(i_{sp})_0$[b] | $(E_p)_c$[b] | $E_\lambda$[b] | |
| 0.04 | 8 | 9.8 | 5.8 | 5.5 | −0.52 | −0.63 | 0.014 |
| 0.02 | 8 | 6.9 | 3.6 | 3.3 | −0.52 | −0.64 | 0.018 |
| 0.01 | 8 | 4.6 | 2.2 | 1.7 | −0.50 | −0.60 | 0.019 |
| 0.04 | 12 | 9.1 | 4.6 | 5.2 | −0.54 | −0.65 | 0.033 |
| 0.02 | 12 | 6.2 | 3.0 | 2.9 | −0.53 | −0.64 | 0.026 |
| 0.01 | 12 | 4.1 | 1.5 | 1.4 | −0.52 | −0.64 | 0.029 |
| 0.04 | 15 | 10.0 | 5.7 | 5.3 | −0.53 | −0.63 | 0.032 |
| 0.02 | 15 | 6.5 | 3.1 | 2.5 | −0.52 | −0.64 | 0.033 |
| 0.01 | 15 | 4.2 | 1.6 | 0.8 | −0.52 | −0.64 | 0.038 |
| 0.20 | 21 | 25.1 | 14.6 | 13.5 | −0.57 | −0.69 | 0.089 |
| 0.04 | 21 | 9.9 | 4.2 | 3.4 | −0.53 | −0.64 | 0.092 |
| 0.02 | 21 | 6.0 | 2.1 | 1.1 | −0.51 | −0.62 | 0.098 |
| 0.20 | 23 | 26.5 | 14.9 | 14.6 | −0.56 | −0.67 | 0.109 |
| 0.10 | 23 | 17.6 | 9.1 | 8.5 | −0.53 | −0.63 | 0.107 |
| 0.04 | 23 | 9.8 | 4.1 | 3.4 | −0.51 | −0.60 | 0.107 |

[a] Solution of $[Cr(bipy)_3]^{3+}$ in 0.1 *M* potassium chloride at pH 5. [b] Reference 8.

waves were observed at more cathodic potentials as shown in Figure 1.

The black suspension obtained after a 3-electron/molecule reduction was transferred under argon to a $10^{-1}$ *M* potassium chloride solution saturated with oxygen and through which oxygen was continuously bubbled. The black suspension immediately converted to a yellow solution. The polarogram of this yellow solution shown in Figure 1 was very similar to the polarogram of the original tris complex taken before any electrolysis. In addition, the ultraviolet spectrum of this solution was the same as that of the tris complex. Thus, the product of the three-electron reduction of the tris complex, which is probably $[Cr(bipy)_3]^0$, can be oxidized to give the original tris chromium(III) complex.

To confirm the results of the polarography and controlled-potential electrolysis and to substantiate further the reaction mechanism described by eq 1–4, a cyclic voltammetric study was made of the $[Cr(bipy)_3]^{3+}$ complex. Cyclic voltammograms taken between −0.2 and −0.6 V at various scan rates showed a single cathodic and a single anodic peak. A diagnostic test described by Nicholson[8] in which the ratios of anodic to cathodic peak currents are plotted as a function of the scan rate indicated a reversible charge transfer followed by an irreversible chemical reaction. The reaction in eq 2 is itself reversible, but when, as in the cyclic voltammetry experiments, $[Cr(bipy)_2(H_2O)_2]^{2+}$ is formed in the presence of $[Cr(bipy)_3]^{3+}$, the diaquo complex is very rapidly removed from the solution *via* the electron-exchange reaction described in eq 3. Under these conditions, then, reaction 2 appears irreversible.

Table I shows typical cyclic voltammetric data obtained from a solution of $[Cr(bipy)_3]^{3+}$ at pH 5 and varying temperatures. Utilizing the measured current values, the ratio of anodic to cathodic current was calculated at various scan rates and temperatures. Although the product of reaction 2 is electroactive at the potentials where the peak currents were measured, it is present only in very small concentrations due to the fact that it is very rapidly consumed according to reaction 3 and as a result the portion of the peak currents due to this substance was negligible. These peak currents were then compared to Nicholson's[8] tabulated values of the ratio of anodic to cathodic peak currents *vs.* the $k_f\tau$ value (where $k_f$ is the rate constant of the irreversible chemical reaction and $\tau$ 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 at various temperatures. The values were as follows: 8°, 0.017; 12°, 0.029; 15°, 0.034; 21°, 0.093; 23°, 0.108 sec$^{-1}$. An Arrhenius plot of these rate constants was performed and the least-squares line through the points has a correlation coefficient of 0.96. From the slope of the plot an activation energy, $E_A$, of 20.3 ± 0.8 kcal was calculated. Baker[5] reported an activation energy of 22.6 ± 0.5 kcal. He did not, however, stipulate the pH at which the measurements were made. Reported activation energies (kcal) for similar complexes in a ligand-exchange reaction are as follows: $[Co(phen)_3]^{2+}$, 21; $[Ni(bipy)_3]^{2+}$, 21.8; $[Fe(phen)_3]^{2+}$, 20.[5]

**Diaquobis(2,2′-bipyridine)chromium(III) Ion and Bipyridine.**—It is now quite clear from the experimental data that a slight reduction of the $[Cr(bipy)_3]^{3+}$ complex produces a solution containing equimolar amounts of $[Cr(bipy)_2(H_2O)_2]^{3+}$ and bipyridine. Electrolysis of this solution at a potential of −0.80 V was described in the preceding section. Polarographic and spectrophotometric data indicated that $[Cr(bipy)_3]^{2+}$ was the only major species present after electrolysis. The presence of this species can be explained if one reexamines reactions 1–4. The value for $k_2$ has been calculated from equilibrium[12] and kinetic[13] data and is of the order of $10^3$ sec$^{-1}$. Our calculated value for $k_1$ is approximately $10^{-1}$ sec$^{-1}$ which suggests an equilibrium constant for reaction 2 of about $10^{-4}$.

Although $[Cr(bipy)_3]^{2+}$ is the initial product of the reduction of $[Cr(bipy)_3]^{3+}$, it is not observed as the final product if the first one-electron reduction is carried out at a potential less than about −0.65 V. This is due to the fact that $[Cr(bipy)_3]^{2+}$ formed in the reduction equilibrates with $[Cr(bipy)_2(H_2O)_2]^{2+}$ which in turn reacts with unreduced $[Cr(bipy)_3]^{3+}$ according to reaction 3. The result of this, of course, is a solution containing, almost exclusively, $[Cr(bipy)_2(H_2O)_2]^{3+}$. Baker[5] has postulated that $k_3$ is of the order of $10^5$ $M^{-1}$ sec$^{-1}$ and $k_4$ is negligible; therefore, reduction of $[Cr(bipy)_2(H_2O)_2]^{3+}$ in the presence of bipyridine as

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(12) A. M. Zwickel and H. Taube, *Discuss. Faraday Soc.*, **29**, 42 (1960).

(13) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, **86**, 1019 (1964).

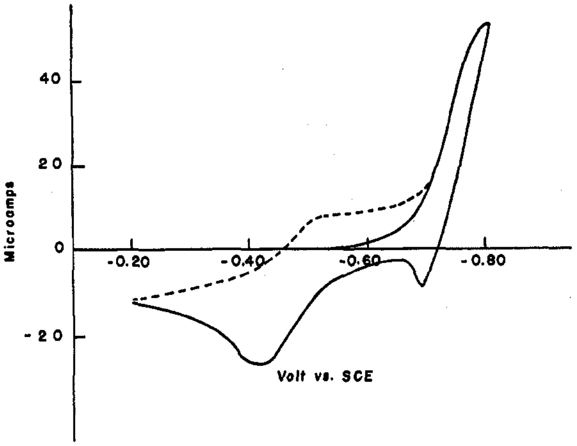

Figure 4.—Cyclic voltammogram of 1.4 × $10^{-3}$ *M* $[Cr(bipy)_2(H_2O)_2]^{3+}$ and 2,2′-bipyridine at a scan rate of 0.1 V/sec, pH 6.5, 26°, and 0.1 *M* potassium chloride.

described in the preceding section will produce $[Cr(bipy)_3]^{2+}$ according to the reactions

$$[Cr(bipy)_2(H_2O)_2]^{3+} + e^- \rightleftarrows [Cr(bipy)_2(H_2O)_2]^{2+} \qquad E_{1/2} = 0.72\ V \quad (4)$$

$$[Cr(bipy)_2(H_2O)_2]^{2+} + bipy \underset{k_1}{\overset{k_2}{\rightleftharpoons}} [Cr(bipy)_3]^{2+} + 2H_2O \quad (5)$$

We sought to confirm our conclusions derived from the spectrophotometric, polarographic, and electrolysis experiments by studying the cyclic voltammetric behavior of a mixture of $[Cr(bipy)_2(H_2O)_2]^{3+}$ and 2,2′-bipyridine. A typical cyclic voltammogram is shown in Figure 4. The cathodic switching potential was necessarily close to the peak potential due to the presence of another cathodic peak just beyond −0.80 V. The first sweep showed a single cathodic peak at −0.82 V and two anodic peaks at −0.70 and −0.43 V. On the next and all subsequent sweeps, a second cathodic peak was observed at −0.51 V. Cyclic voltammograms of this type are typical of a system where a chemical reaction is coupled between two transfers. In this case the cathodic peak at −0.82 V was due to reduction of $[Cr(bipy)_2(H_2O)_2]^{3+}$ and the anodic peak at −0.70 V was the reverse or oxidation of the chromium(II) ion. After reduction, the bis complex reacted with the bipyridine in solution giving the tris complex whose oxidation was observed at −0.43 V. The cathodic wave at −0.51 V, which was not observed on the first cathodic sweep, was due to reduction of $[Cr(bipy)_3]^{3+}$ which was not present during the first cathodic sweep. The anodic and cathodic peaks at −0.43 and −0.51 V were very nearly at the same positions as those obtained from solutions of the tris complex when similar scan rates were used.

The solution of bipyridine and $[Cr(bipy)_2(H_2O)_2]^{3+}$ was next reduced a total of 1 electron/molecule at −0.80 V. Following the reduction, the solution became deep red possessing visible absorption maxima at 562 and 467 nm, respectively. The polarogram of the solution was identical with that shown in Figure 1B. Earlier it was shown that the anodic wave at −0.50 V was due to oxidation of the $[Cr(bipy)_3]^{2+}$ in solution. Using the previously calculated diffusion current constant for this wave, it was determined that the concentration of $[Cr(bipy)_3]^{2+}$ equaled that of the original $[Cr(bipy)_2(H_2O)_2]^{3+}$.

Oxidation of the reduced solution was attempted in order to transform all of the $[Cr(bipy)_3]^{2+}$ into the corresponding chromium(III) complex. This latter complex had previously been characterized spectrally and electrochemically and thus its presence in solution could be unequivocally verified. Rapid oxidation with oxygen gas was accomplished by slowly transferring the reduced solution to a 0.1 *M* potassium chloride solution saturated with oxygen gas and through which oxygen gas was continuously bubbling. The transfer was accomplished within an inert atmosphere of argon. As the deep red reduced solution came in contact with the oxygen-saturated solution, it became yellow. A uv spectrum of the yellow solution was identical with a uv spectrum of $[Cr(bipy)_3]^{3+}$. After removal of oxygen from the solution, the pH was adjusted to 3.5 and a polarogram identical with that of Figure 1A was recorded. Polarographic and cyclic voltammetric examination of this solution as a function of temperature and pH confirmed that the solution was that of $[Cr(bipy)_3]^{3+}$.

Other oxidation methods including the addition of oxygen gas or air to the reduced solution, the exposure of the reduced solution to the ambient atmosphere, or electrical oxidation at −0.30 V were attempted. These produced the same results: an orange solution containing free bipyridine whose polarogram was identical with that shown in Figure 2A. These slow oxidations occur in the presence of relatively large concentrations of reduced materials which are predominantly $[Cr(bipy)_3]^{2+}$ and small equilibrium concentrations of $[Cr(bipy)_2(H_2O)_2]^{2+}$. The $[Cr(bipy)_3]^{3+}$ formed by oxidation of the $[Cr(bipy)_3]^{2+}$ rapidly undergoes an electron exchange according to eq 3. The net result of the slow oxidation is conversion of all $[Cr(bipy)_3]^{2+}$ into $[Cr(bipy)_2(H_2O)_2]^{3+}$ and free bipyridine. In the rapid-oxidation method, the $[Cr(bipy)_3]^{3+}$ formed is in a solution void of other reduced materials and thus once formed will not be depleted by reaction according to eq 4 and the result of the oxidation will be production of $[Cr(bipy)_3]^{3+}$.

**Diaquobis(2,2′-bipyridine)chromium(III) Ion.**—$[Cr(bipy)_2(H_2O)_2]^{3+}$ was prepared *in situ* from $[Cr(bipy)_3]^{3+}$. A solution of the tris complex was electrolyzed at −0.60 V at a stirred mercury pool. As described earlier, only about 0.06 electron/molecule could be added at this potential at 25°. At this point the solution consisted essentially of $[Cr(bipy)_2(H_2O)_2]^{3+}$ and free bipyridine. The solution was extracted several times with chloroform to remove the free bipyridine. The remaining aqueous solution was orange and its ultraviolet absorption spectrum exhibited two absorption maxima at 248 and 308 nm. A polarogram of the solution remaining after extraction and shown in Figure 2 was identical with one taken before extraction except at very cathodic potentials where free bipyridine could also be reduced polarographically.

The cyclic voltammogram of this solution of $[Cr(bipy)_2(H_2O)_2]^{3+}$ was similar to that obtained for this complex in the presence of bipyridine as shown in Figure 4. A single cathodic peak at −0.80 V and two anodic peaks at −0.60 and −0.40 V were observed on the first sweep. On subsequent sweeps, a second cathodic wave was observed with $E_p$ = −0.50 V. This new cathodic peak occurred at the same potential (when using similar scan rates) as the peak due to the reduction of $[Cr(bipy)_3]^{3+}$ to $[Cr(bipy)_3]^{2+}$ as discussed earlier.

When a solution of the bis complex was electrolyzed at −0.80 V, 1 electron/molecule could be passed. The resulting solution was deep red with visible absorption maxima at 470 and 562 nm. A polarogram of this solution is shown in Figure 2. The limiting diffusion current of the anodic wave at $E_{1/2} = -0.49$ V was half that of the original cathodic wave at −0.72 V. The appearance of an anodic wave at $E_{1/2} = -0.49$ V after a one-electron reduction was described previously for solutions of this complex in the presence of free bipyridine. In the previous case, however, the limiting diffusion current of the anodic wave appearing after electrolysis was *equal* to that for the cathodic wave at −0.72 V. The appearance of the anodic polarographic wave at −0.49 V in the reduced solution was apparently due to $[Cr(bipy)_3]^{2+}$. This assumption is based on the position of the anodic wave and the visible absorption spectrum of the reduced solution. In order to substantiate this assumption, the reduced solution was rapidly oxidized with oxygen gas as described previously, in the anticipation of obtaining $[Cr(bipy)_3]^{3+}$ from the $[Cr(bipy)_3]^{2+}$ of the reduced solution. On contact with the oxygen-saturated solution, the reduced solution became yellow and after adjusting the solution to pH 3.5, the polarogram shown in Figure 2 was obtained. It contained a cathodic wave with $E_{1/2}$ of −0.49 V. The polarographic and cyclic voltammetric response to the solution between −0.20 and −0.80 V, as a function of temperature and pH, were similar to those previously observed for a solution of $[Cr(bipy)_3]^{3+}$ under similar conditions.

The above experiments showed conclusively the presence of $[Cr(bipy)_3]^{2+}$ in a solution of $[Cr(bipy)_2(H_2O)_2]^{3+}$ which had been electrolyzed by 1 electron/molecule at −0.80 V. Since no free bipyridine was initially available when the $[Cr(bipy)_2(H_2O)_2]^{3+}$ was reduced, the $[Cr(bipy)_3]^{2+}$ must have been formed by ligand exchange between two molecules of the bis complex forming a tris and a mono complex. The suggested reaction sequence is described by reactions 6–8.

$$[Cr(bipy)_2(H_2O)_2]^{3+} + e^- \rightleftarrows [Cr(bipy)_2(H_2O)_2]^{2+} \quad E = -0.72 \text{ V} \tag{6}$$

$$[Cr(bipy)_2(H_2O)_2]^{2+} + 2H_2O \rightleftharpoons [Cr(bipy)(H_2O)_4]^{2+} + bipy \tag{7}$$

$$[Cr(bipy)_2(H_2O)_2]^{2+} + bipy \rightleftharpoons [Cr(bipy)_3]^{2+} + 2H_2O \tag{8}$$

The equilibrium constant for reaction 8 has been shown earlier to be about $10^4$. We have not definitely established that the ligand exchange produces only the mono complex, $[Cr(bipy)(H_2O)_4]^{2+}$. Although it is conceivable that some $[Cr(H_2O)_6]^{2+}$ could also be formed, the data presently available suggest this is not the case. It would seem that one conclusive test would be to determine the amount of tris complex formed by reaction 8. If reaction 7 is correct, we should obtain as a maximum half as much $[Cr(bipy)_3]^{2+}$ as we had $[Cr(bipy)_2(H_2O)_2]^{3+}$ initially. If the ligand-exchange reaction results in formation of $[Cr(H_2O)_6]^{2+}$, we should obtain as a maximum two-thirds as much $[Cr(bipy)_3]^{2+}$ as we had $[Cr(bipy)_2(H_2O)_2]^{3+}$ initially. As stated earlier the anodic wave at $E_{1/2} = -0.49$ V resulting from the reduction of $[Cr(bipy)_3]^{3+}$ gave a diffusion current constant of 1.25 for the $[Cr(bipy)_3]^{2+}$ species. Using this value the concentration ratio of $[Cr(bipy)_3]^{2+}$ to original $[Cr(bipy)_2(H_2O)_2]^{3+}$ was calculated to be 0.5:1. This ratio definitely suggests that the products of the reduction are the tris and the mono complexes.

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# Electron Spin Resonance Active Molybdenum(V) Complexes in Dimethylformamide

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Complexes of molybdenum(V) with 8-hydroxy-, 8-mercapto-, and 8-aminoquinoline and 3,4-dimercaptotoluene in anhydrous dimethyformamide have been investigated. Each ligand forms a 100% esr active complex in the ratio 1:1 (ligand to Mo(V)). The *g* values and hyperfine splittings and the visible absorption bands have been determined and the formation constants estimated for each complex. The results indicate the affinity of Mo(V) for ligands of comparable structure is $S^- > O^- > NH_2$ and suggest considerable electron delocalization for the thiol complexes. Possible implications for molybdenum containing enzymes are discussed.

## Results

Recently, esr signals attributed to molybdenum(V) have been reported for a number of enzyme systems.[1–3] Because of this, there is considerable interest in model esr active molybdenum(V) complexes. In aqueous solution, however, Mo(V) complexes generally exist as esr inactive dimers, sometimes in equilibrium with rather small amounts of esr active species (monomers or triplets).[4–6] In certain polar, nonaqueous solvents,

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