Cu(3-C.P.)$_2$ClO$_4$: 690, 645, 622, 548, 510 (vw), 473, 455, 408, 397. Ag(3-C.P.)$_3$ClO$_4$: 692, 640, 622, 552, 543 (red shoulder), 513 (vw), 482, 470, 400, 395. Ag(3-C.P.)$_2$ClO$_4$: 695, 652, 622, 557, 547, 480, 470, 405, 394. Au(3-C.P.)$_2$ClO$_4$: 687, 670, 666, 622, 559, 546, 480, 472, 422, 413. 2-Cyanopyridine: 630, 545 (br), 358 (w), 347 (w). Cu(2-C.P.)$_2$ClO$_4$: 637, 622, 553, 542, 525, 408, 395 (red shoulder), 367 (w), 347 (w). Ag(2-C.P.)$_2$ClO$_4$: 641, 620, 551, 548, 482, 408, 396 (red shoulder), 367 (w), 355 (w). Au(2-C.P.)$_2$ClO$_4$: 622, 559, 543, 496, 440, 413 (w), 397 (w), 370 (w), 350 (w).

All the metal perchlorate complexes have a band at approximately 620 cm.$^{-1}$, which is attributable to ν_4 of the perchlorate anion.[16] The one-to-one correspondence of the spectra of the 4-cyanopyridine complexes with that of 4-cyanopyridine indicates that the metal–nitrogen frequency is below 300 cm.$^{-1}$. In the case of the 3-cyanopyridine complexes, a new peak appears between 640 and 670 cm.$^{-1}$. However, in light of the absence of a new band in this region for the 4-cyanopyridine complexes and because the stability of the 4-cyanopyridine–silver(I) complex is approximately the same as that of the 3-cyanopyridine–silver(I) complex,[15] it is difficult to justify the assignment of this band to the metal–nitrogen stretching vibration. If π-bonding is involved in the metal–nitrogen bond, it certainly does not strengthen the bond sufficiently so that the metal–nitrogen stretching band occurs above 300 cm.$^{-1}$. These observations are consistent with the results obtained by Gill, *et al.*,[12] for pyridine complexes.

In the 2-cyanopyridine complexes the metal ions are coordinated to the nitrile nitrogen. Lott[11] has examined the far-infrared spectra of benzonitrile complexes of transition metal ions and has shown that the new band in the 480–520 cm.$^{-1}$ region is due to the metal ion–nitrile nitrogen stretching vibration. The far-infrared spectra of the 2-cyanopyridine complexes of copper(I), silver(I), and gold(I) also show a new absorption band in this region.

Basicity of the Cyanopyridines.—The order of basicity of the three cyanopyridines with respect to perchloric acid in glacial acetic acid has been shown by potentiometric titration data to be 4-cyanopyridine $>$ 3-cyanopyridine $\gg$ 2-cyanopyridine. The basicity of 2-cyanopyridine is so low that it cannot be titrated with perchloric acid. The latter situation can be attributed to the steric problem of placing the acetic acid solvated proton adjacent to the nitrile group. Brown[17] has shown that steric effects are marked in *ortho*-substituted pyridines and the extent of the effects depends on the size of the acid group. The difference in basicity between 4- and 3-cyanopyridine is due to the lower electron density at the ring nitrogen in 3-cyanopyridine than in 4-cyanopyridine because of the greater electron withdrawal effect of the nitrile group in the 3- position than in the 4- position.

Acknowledgment.—We wish to acknowledge the generous support of the Directorate of Chemical Sciences, Air Force Office of Scientific Research (AFOSR Grant 220-63), the University of Kansas (General Research Fund), and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

[16] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 167.

[17] H. C. Brown, *J. Chem. Educ.*, **36**, 424 (1959).

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Polarography and Oxidation–Reduction Reactions of the Chromium(II) and Chromium(III) Complexes of 2,2′-Bipyridine

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Tris(2,2′-bipyridine)chromium(III) is reduced reversibly in a one-electron reduction to Cr(bipy)$_3^{2+}$ at the dropping mercury electrode at −0.49 v. A second wave at −0.72 v. is attributed to the reversible one-electron reduction of Cr(bipy)$_2$(H$_2$O)$_2^{3+}$ formed at the electrode surface from Cr(bipy)$_3^{3+}$, the dissociation of which is catalyzed by Cr(bipy)$_3^{2+}$ formed at −0.49 v. The rate law for the homogeneous catalytic dissociation of Cr(bipy)$_3^{3+}$ in the presence of Cr(bipy)$_3^{2+}$ is $d[\mathrm{Cr(bipy)_3^{3+}}]/dt = -k_1[\mathrm{Cr(bipy)_3^{2+}}]$, where k_1 is the rate of dissociation of Cr(bipy)$_3^{2+}$ with a value of 0.38 sec.$^{-1}$ at 25° and an activation energy of 22.6 kcal. Chemical oxidation of Cr(bipy)$_3^{2+}$ by Co(bipy)$_3^{3+}$, I$_2$, and O$_2$ produces Cr(bipy)$_2$(H$_2$O)$_2^{3+}$ in a reaction that may proceed first to Cr(bipy)$_3^{3+}$ which is catalytically dissociated to the diaquo species in the presence of unreacted Cr(bipy)$_3^{2+}$.

Introduction

There have been conflicting reports in the literature regarding the mechanism of the oxidation of the tris(2,2′-bipyridine)chromium(II) ion and the nature of the chromium(III) products. Zwickel and Taube[2] determined the successive formation constants for the

[1] To whom correspondence should be addressed.

[2] A. M. Zwickel and H. Taube, *Discussions Faraday Soc.*, **29**, 42 (1960).

mono, bis, and tris complexes and used $Cr(bipy)_3^{2+}$ as a model reductant for a kinetic study with $Co(NH_3)_6^{3+}$ as oxidant. The kinetic results were consistent with an outer-sphere oxidation to $Cr(bipy)_3^{3+}$. Waind and Murray[3] reported, however, that oxidation of $Cr(bipy)_3^{2+}$ by $Co(NH_3)_6^{3+}$ produces $Cr(bipy)_2(H_2O)_2^{3+}$ or its conjugate bases instead.

Vlcek[4] studied the polarographic behavior of $Cr(bipy)_3^{3+}$, obtaining waves at −0.36, −0.73, and −1.38 v. (*vs.* s.c.e.) corresponding to three one-electron reductions. The species $Cr(bipy)_3^{2+}$, $Cr(bipy)_3^{+}$, and $Cr(bipy)_3$ were generated by a commutator technique and polarograms obtained therefrom were consistent with the waves observed for reduction of $Cr(bipy)_3^{3+}$.

Since preliminary results of the present work revealed a marked departure from the results of Vlcek a study was made of the polarograms of $Cr(bipy)_3^{3+}$, $Cr(bipy)_2(H_2O)_2^{3+}$, and $Cr(bipy)_3^{2+}$ as a function of concentration, pH, and temperature. The kinetics of the homogeneous dissociation of $Cr(bipy)_3^{3+}$ and the oxidation products of $Cr(bipy)_3^{2+}$ were then studied using polarographic analytical methods.

Experimental

Reagents.—Solutions of $Cr(aq)^{2+}$ were prepared by electrolytic reduction of solutions of chromium(III) perchlorate in aqueous perchloric acid under an atmosphere of nitrogen in an apparatus similar to that described by Pecsok and Schaefer.[5] Solutions were analyzed periodically by titration with cerium(IV) solutions using ferroin as an indicator and were dispensed either by a buret system or by hypodermic syringe. All reagents used were of reagent grade without further purification.

Preparation of Compounds.—Tris(2,2'-bipyridine)chromium(III) perchlorate was prepared by adding 10 ml. of 0.2 *M* $Cr(aq)^{2+}$ in 0.1 *M* $HClO_4$ to a deoxygenated suspension of 2 g. of 2,2'-bipyridine in 90 ml. of water at pH 2. The black suspension of $Cr(bipy)_3(ClO_4)_2$ thus obtained was bubbled with oxygen for 1 hr. until the black solid became yellow. The yellow solid was filtered, washed with ethanol and water, recrystallized from water, and dried over H_2SO_4.

Anal.[6] Calcd. for $Cr(C_{10}H_8N_2)_3(ClO_4)_3 \cdot {}^1/_2H_2O$: C, 43.58; H, 3.02; N, 10,16; Cl, 12.77. Found: C, 43.87; H, 3.23; N, 10.09; Cl, 12.08.

Absorption spectra, taken on a Cary recording spectrophotometer, showed maxima (log ϵ_M in parentheses) at 280 (4.15) and 308 mμ (4.29) with a shoulder at 345 mμ (3.71). The spectra showed only minor changes on acidification with HCl. Dihydroxobis(2,2'-bipyridine)chromium(III) perchlorate was prepared from the filtrate in a procedure similar to that for $Cr(bipy)_3(ClO_4)_3$ but at a pH of 4. A yellow solid obtained in this procedure also analyzed for $Cr(bipy)_3(ClO_4)_3$. The filtrate, after the removal of the yellow solid, was concentrated on a hot plate. On cooling, red crystals separated. These were washed with water and ethanol, recrystallized from water, and dried over H_2SO_4.

Anal. Calcd. for $Cr(C_{10}H_8N_2)_2(OH)_2ClO_4$: C, 47.43; H, 3.77; N, 11.06; Cl, 7.01. Found: C, 47.97; H, 3.56; N, 10.93; Cl, 9.72.

Absorption spectra (log ϵ_M in parentheses) showed bands at 305–315 (4.53) and 515 mμ (0.86). On acidification with HCl the solution became yellow and the 515 mμ band shifted to 480 mμ. These spectra are similar to those reported by Inskeep and Bjerrum[7] for $Cr(bipy)_2(OH)_2ClO_4$.

Polarography.—Polarograms were obtained on a Sargent Model XV recording polarograph using an H-type cell with a sintered glass disk and agar plug separating the saturated calomel electrode from the dropping mercury electrode. A solution of 0.5 *M* NaCl without maximum suppressor was the supporting electrolyte in all experiments.

One polarogram of $Cr(bipy)_3^{3+}$ determined on a Fisher Electropode gave values of the half-wave potential identical with those of the Sargent instrument. For calibration, polarograms were obtained periodically on solutions of Cd^{2+}.

Temperature control at 26° was better than 0.05°, that at other temperatures was about 0.5°. Values of the mass of mercury per second, *m*, and the drop time, *t*, unless stated otherwise, were 1.55 mg. sec.$^{-1}$ and 4.68 sec., respectively, in 0.5 *M* NaCl over the range of applied potentials −0.4 to −0.6 v.

Solutions of $Cr(bipy)_3^{2+}$ were prepared *in situ* by adding a measured volume of standard $Cr(aq)^{2+}$ to a deoxygenated suspension of 2,2'-bipyridine in NaCl solution in the cell. Solutions of other complexes were prepared by dissolving a weighed quantity of the solid in a measured volume of NaCl solution. The concentration of $Cr(bipy)_3^{2+}$ was determined polarographically. Polarographic standards for this determination were obtained by running polarograms of $Cr(bipy)_3^{2+}$, then titrating the solution with a standard solution of $Co(bipy)_3^{3+}$, following the end point by the measurement of the anodic current of $Cr(bipy)_3^{2+}$ at −0.3 v. and by a visual observation of the disappearance of the purple color of the chromium(II) complex. The end points determined by the two methods agreed to within 2%. The concentration of $Cr(bipy)_3^{2+}$ determined by titration was usually 5–10% lower than the amount of chromium(II) added, indicating some oxidation during the complex formation. The pH was adjusted with $HClO_4$ or NaOH.

Kinetic Measurements.—The dissociation rate of $Cr(bipy)_3^{3+}$ was measured by following the limiting current, $i_{L(1)}$, at −0.65 v. with time. Solutions of $Cr(bipy)_3^{2+}$ were prepared in the polarograph cell and the polarogram was recorded. An appropriate volume of a deoxygenated solution of $Cr(bipy)_3^{3+}$ was then added and $i_{L(1)}$ was recorded as a function of time. Following the completion of the reaction the polarogram was recorded again. No change in the anodic current of $Cr(bipy)_3^{2+}$ was ever observed. The final polarograms were consistent with a solution of $Cr(bipy)_3^{2+}$ and $Cr(bipy)_2(H_2O)_2^{3+}$. Concentrations of all complex species were determined from limiting currents. Blank runs without chromium(II) showed no change in the polarograms over long periods of time.

Chemical Oxidation of $Cr(bipy)_3^{2+}$.—Solutions of $Cr(bipy)_3^{2+}$ were prepared in the polarograph cell and the polarograms recorded. Standard solutions of oxidant were then added slowly with stirring by N_2. The anodic current of $Cr(bipy)_3^{2+}$ was measured after each addition of oxidant. Following the titration, the pH was adjusted to 2.0 and the polarogram was again determined as a qualitative and quantitative analysis of the product solution.

Results

Polarography.— Reduction of $Cr(bipy)_3^{3+}$ proceeds in four steps at 26° and pH 4 with half-wave potentials at −0.49, −0.72, −0.90, and −1.28 v. *vs.* s.c.e. Current–voltage curves as a function of pH are shown in Figure 1 and the limiting current ratio of the first to second wave is shown in Figure 2. The first wave is reversible with a half-wave potential and limiting current independent of pH over a wide range and independent of free bipyridine concentration in the range 0–2 × 10^{-3} *M*. The half-wave potential and limiting current of the second wave are independent of pH in the range 1.5–5 but the limiting current decreases above

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(3) G. M. Waind and R. Murray, Proceedings of the Seventh International Conference on Coordination Chemistry, Stockholm, 1962, p. 309.

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

(5) R. L. Pecsok and W. P. Schaefer, *J. Am. Chem. Soc.*, **83**, 62 (1961).

(6) Microtech Laboratory, Skokie, Ill.

(7) R. G. Inskeep and J. Bjerrum, *Acta Chem. Scand.*, **15**, 62 (1961).

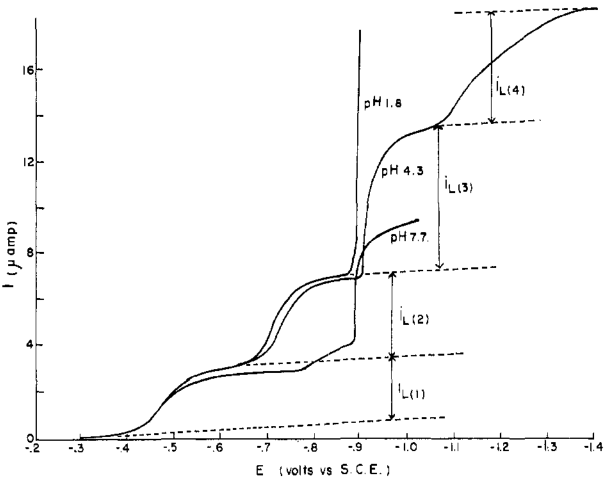

Figure 1.—Polarograms of $Cr(bipy)_3(ClO_4)_3$ (3.1 m*M*) as a function of pH in 0.5 *M* NaCl without excess bipyridine at 26°.

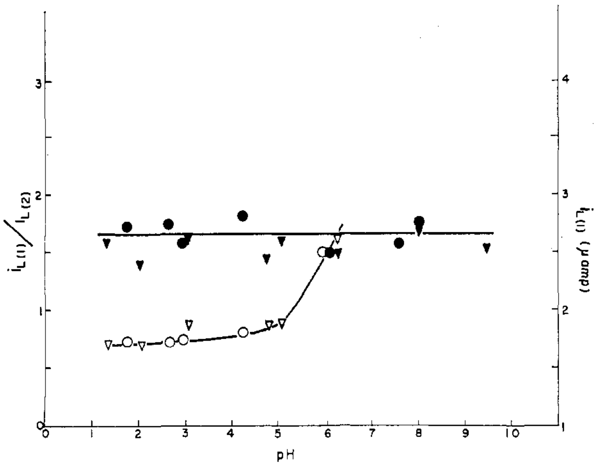

Figure 2.—Limiting current, at 26°, of the first cathodic wave of $Cr(bipy)_3(ClO_4)_3$ (right-hand ordinate, closed circles and triangles) and ratio of the first and second cathodic waves of $Cr(bipy)_3(ClO_4)_3$ (left-hand ordinate, open circles and triangles) as a function of pH. Circles represent solutions containing no excess of bipyridine, triangles represent solutions saturated in bipyridine at pH 4 (*ca.* 10 m*M*).

pH 5. At pH lower than 4 the limiting current of the third wave is very high, owing, presumably, to a catalytic hydrogen effect. The fourth wave is drawn out and poorly defined. The characteristics of the third and fourth waves were not studied in detail.

The diffusion current constant, $I = 706nD^{1/2}$, where n is the number of electrons transferred and D is the diffusion coefficient, is 1.28 for the combined first and second waves. For purposes of comparison, the diffusion current constant of $Co(bipy)_3{}^{3+}$ is 1.3. This similarity of the diffusion current constants as well as the approximate equality of the wave heights of the combined first and second waves with the third and fourth waves suggest that the first two waves result from two related chromium(III) species.

The sum, $i_{L(1)} + i_{L(2)}$, is a linear function of concentration in the range 0–10 m*M* at pH 2 and 26°. The ratio, $i_{L(1)}/i_{L(2)}$, is constant in this range.

The effect of temperature on the first and second waves of $Cr(bipy)_3{}^{3+}$ at pH 2 is shown in Figure 3. The first wave disappears at higher temperature and the second wave disappears at lower temperature. The half-wave potential of the first wave becomes slightly more positive with an increase in temperature, from −0.51 v. at 1° to −0.48 v. at 40°. Such a shift is characteristic either of a reversible wave with a positive temperature coefficient or an irreversible wave with a very low activation energy.[8] The most interesting feature of the temperature effect, however, is that the temperature coefficient of $i_{L(1)} + i_{L(2)}$, $d \ln i/dT$, is 1.6% deg.$^{-1}$ at 25°, close to that value usually found for diffusion-controlled transport of electroactive species to the surface of a dropping mercury electrode.[9] The ratio $i_{L(1)}/i_{L(2)}$ thus changes markedly with temperature, but the sum $i_{L(1)} + i_{L(2)}$ is a linear function of temperature in the range 1–60°, behaving much as a single, normal diffusion current. Furthermore, rapid changes in temperature result in a rapid adjustment of $i_{L(1)}/i_{L(2)}$ to its new value and these changes are completely reversible, that is, a current–voltage curve taken at 26° is the same after heating at 60° for 10 min. as it was before heating. If the supposition that the first two waves are due to two related chromium(III) species is correct, the temperature effect would suggest that the two species do not exist in the bulk of the solution together. If they did co-exist, related by a rapidly established equilibrium, only one wave at −0.49 v. would be observed, since the less easily reduced species would rapidly be converted into the more easily reduced one as the latter is depleted at the electrode surface. If, on the other hand, the equilibrium between the two coexisting species was slowly established, two waves might be observed, but the limiting current ratio $i_{L(1)}/i_{L(2)}$ would not be expected to respond as rapidly to temperature changes as it is observed to. Furthermore, at low temperatures, two waves would be expected as

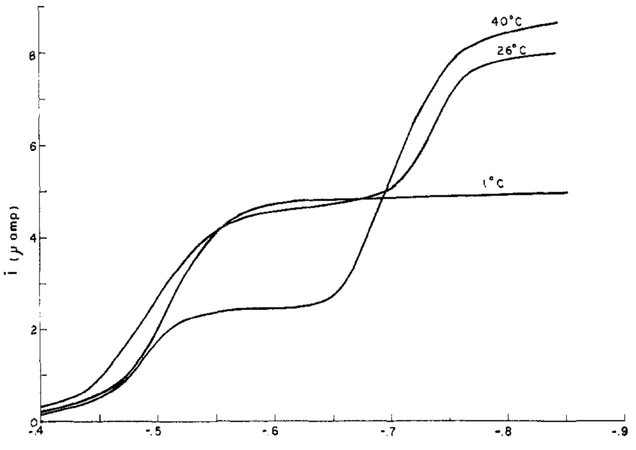

Figure 3.—Polarograms of the first two cathodic waves of $Cr(bipy)_3{}^{3+}$ as a function of temperature at pH 2.0.

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[8] A. A. Vlcek, *Progr. Inorg. Chem.*, **5**, 234 (1963).

[9] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, New York, N. Y., 1952, Vol. 1, p. 90.

the rate of establishment of equilibrium is reduced, whereas at higher temperatures only the wave of the more easily reduced species (−0.49 v.) would be observed as the rate of establishment of the equilibrium is increased. The opposite effect is observed, however. The conclusion remaining is that the two species do not exist together in the bulk of the solution, but that a single species reaches the electrode surface by diffusion, then is converted into a second species by a secondary reaction.

Support for the foregoing supposition and an assignment of the waves for $\mathrm{Cr(bipy)_3^{3+}}$ is suggested by an examination of the current–voltage curves of $\mathrm{Cr(bipy)_3^{2+}}$ and $\mathrm{Cr(bipy)_2(H_2O)_2^{3+}}$. That for $\mathrm{Cr(bipy)_3^{2+}}$ is shown in Figure 4 at pH 2 and 4 at 26°. Between pH 6 and 3 the anodic half-wave potential and limiting current of $\mathrm{Cr(bipy)_3^{2+}}$ are independent of pH in solutions saturated with bipyridine. The half-wave potential is −0.52 v. with $I = 1.52$ for the anodic wave and since the predominant species is $\mathrm{Cr(bipy)_3^{2+}}$ this oxidation is ascribed to the reversible reaction, $\mathrm{Cr(bipy)_3^{2+}} \rightarrow \mathrm{Cr(bipy)_3^{3+}} + e^-$. This is consistent with the assignment of the reverse of this reaction to the wave at −0.49 v. for $\mathrm{Cr(bipy)_3^{3+}}$ solutions and also with the polarographic reversibility of this couple.

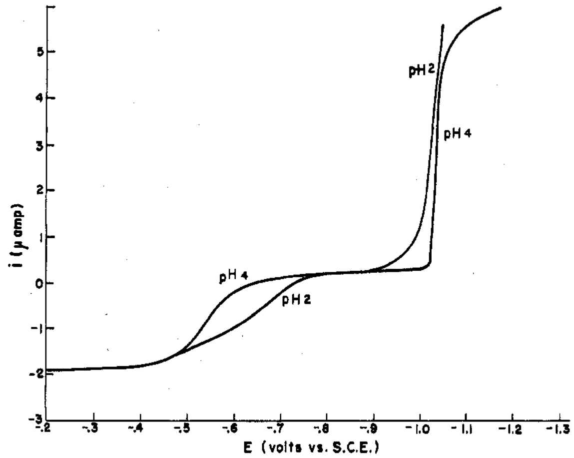

Figure 4.—Polarograms of chromium(II) (0.9 mM) in 0.5 M NaCl saturated with excess bipyridine at 26°.

At low pH (*ca.* 2) the anodic wave of $\mathrm{Cr(bipy)_3^{2+}}$ appears to split into two waves with half-wave potentials estimated to be −0.5 and −0.7 v. This change appears to coincide with the pH at which dissociation of $\mathrm{Cr(bipy)_3^{2+}}$ into $\mathrm{Cr(bipy)_2(H_2O)_2^{2+}}$ is expected to occur, and it is postulated that the wave at −0.7 v. is the anodic wave of the diaquo species.

This postulate is borne out by the current–voltage curve of $\mathrm{Cr(bipy)_2(H_2O)_2^{3+}}$ shown in Figure 5 at pH 2. The first reduction occurs reversibly at half-wave potential −0.72 v. at pH 2, where the diaquo species is expected to be predominant. At higher pH, where hydroxy species are expected, the height of this wave is lower until it disappears above about pH 7. At pH 2 the diffusion current constant for the first wave is 1.1 and the current is a linear function of temperature with a temperature coefficient of 1.3% deg.$^{-1}$ at 25°. The reversibility of the wave supports the assignment of the −0.7-v. anodic wave of chromium(II) at low pH to the oxidation of the diaquo species.

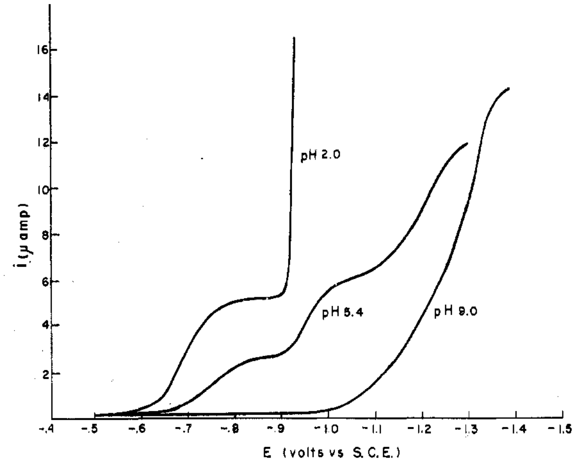

Figure 5.—Polarograms of $\mathrm{Cr(bipy)_2(OH)_2ClO_4}$ as a function of pH at 26° in 0.5 M NaCl with no excess bipyridine.

The coincidence of the cathodic wave for the diaquo chromium(III) species with the anomalous wave at 0.72 v. for $\mathrm{Cr(bipy)_3^{3+}}$ suggests that the latter wave is the result of the dissociation of the tris species at the electrode surface. The conclusion is, therefore, that $\mathrm{Cr(bipy)_3^{3+}}$ is the only species existing in the bulk of the solution containing $\mathrm{Cr(bipy)_3(ClO_4)_3}$, and to account for the dissociation, the following mechanism is propose to occur at the surface of the dropping mercury electrode.

$$\mathrm{Cr(bipy)_3^{3+}} + e^- <==> \mathrm{Cr(bipy)_3^{2+}} \quad E_{1/2} = -0.49 \text{ v.} \tag{1}$$

$$\mathrm{Cr(bipy)_3^{2+}} + 2\mathrm{H_2O} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{Cr(bipy)_2(H_2O)_2^{2+}} + \mathrm{bipy} \tag{2}$$

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

$$\mathrm{Cr(bipy)_2(H_2O)_2^{3+}} + e^- <==> \mathrm{Cr(bipy)_2(H_2O)_2^{2+}} \quad E^{1/2} = -0.72 \text{ v.} \tag{4}$$

The symbol $<==>$ refers to a polarographically reversible reaction at the half-wave potential indicated. The reaction sequence involves the diffusion of $\mathrm{Cr(bipy)_3^{3+}}$ to the electrode surface. Part of this species is then reduced at $E_{1/2} = -0.49$ v., but the remainder is catalytically dissociated to $\mathrm{Cr(bipy)_2(H_2O)_2^{3+}}$, which reduces at $E_{1/2} = -0.72$ v.

The catalysis of the dissociation of $\mathrm{Cr(bipy)_3^{3+}}$ by chromium(II) was demonstrated in the following way. About 1 mM $\mathrm{Cr(bipy)_3^{2+}}$ was added to a 0.1 M solution of $\mathrm{Cr(bipy)_3^{3+}}$ in a deoxygenated spectrophotometer cell. After standing a short time the chromium(II) was air oxidized and the spectrum of the solution was measured. A band was observed at 515 mμ which shifted to 480 mμ on acidification. These bands, which are characteristic of $\mathrm{Cr(bipy)_2(OH)_2^{+}}$ and $\mathrm{Cr(bipy)_2(H_2O)_2^{3+}}$, respectively, were not present before addition of $\mathrm{Cr(bipy)_3^{2+}}$. Oxidation products of $\mathrm{Cr(bipy)_3^{2+}}$ were present in insufficient concentration to cause the bands.

The following treatment is analogous to the reaction layer concept of kinetic currents.[10] Concentrations at the electrode surface are designated by a subscript zero and its absence refers to concentration in the bulk of the solution. A reaction layer of arbitrary thickness, u, is assumed to surround the mercury drop. If the average drop surface area is A the reaction volume is uA. Every $Cr(bipy)_3^{3+}$ entering the reaction volume is assumed to react either by reaction 1 or 3. The rate of change of $[Cr(bipy)_3^{3+}]$ in mmoles sec.$^{-1}$ is $dN_0/dt = k_dA\{[Cr(bipy)_3^{3+}] - [Cr(bipy)_3^{3+}]_0\} - uAk_3[Cr(bipy)_3^{3+}]_0[Cr(bipy)_2^{2+}]_0$. A linear concentration gradient has been assumed for diffusion where k_d is a proportionality constant containing the diffusion coefficient. The reverse of reaction 3 (k_4) is assumed to be negligible. Dissociated species (aquo complexes) have been written without the water molecules for simplification.

In the limit of the limiting current region $[Cr(bipy)_3^{3+}] \gg [Cr(bipy)_3^{3+}]_0$, which leads to

$$dN_0/dt = k_dA[Cr(bipy)_3^{3+}] - uAk_3[Cr(bipy)_3^{3+}]_0[Cr(bipy)_2^{2+}]_0 \quad (5)$$

On application of the steady-state approximation for $[Cr(bipy)_2^{2+}]_0$ eq. 5 becomes

$$dN_0/dt = k_dA[Cr(bipy)_3^{3+}] - uAk_1k_3[Cr(bipy)_3^{3+}]_0[Cr(bipy)_3^{2+}]_0/\{k_2[bipy] + k_3[Cr(bipy)_3^{3+}]_0\} \quad (6)$$

or if $k_3[Cr(bipy)_3^{3+}]_0 \gg k_2[bipy]$

$$dN_0/dt = k_dA[Cr(bipy)_3^{3+}] - uAk_1[Cr(bipy)_3^{2+}]_0 \quad (7)$$

The assumption made regarding the relative rates, k_1, k_2, and k_3, is justified by the independence of $i_{L(1)}/i_{L(2)}$ on bipyridine concentration, by the estimate of k_2 to be about 10^3 from equilibrium[2] and kinetic[11] data, and by the assumption that since $Cr(bipy)_2(H_2O)_2^{2+}$ is a low-spin ground state[12] k_3 is probably of the order of $10^5\ M^{-1}$ sec.$^{-1}$.

From an examination of reactions 1–4 it is apparent that one equivalent of $Cr(bipy)_3^{2+}$ is generated at the electrode surface for every faraday of charge transferred and that every $Cr(bipy)_3^{2+}$ destroyed by reaction 2 is regenerated by reaction 3. Thus $[Cr(bipy)_3^{2+}]_0$ is constant at a given current and is proportional to the current on the plateau of the first wave. The average recorded current is assumed to be equal to the average current flowing during the lifetime of the drop. If the average limiting current is expressed as $\bar{i}_L$ and the mmoles of $Cr(bipy)_3^{2+}$ as N'_0, we have $\bar{i}_{L(1)} = nFN'_0/t$ or $[Cr(bipy)_3^{2+}]_0 = t\bar{i}_{L(1)}/nFuA$ where t is drop time and n and F have their usual significance. Substituting this into eq. 7 and identifying $nF\ dN_0/dt$ with $\bar{i}_{L(1)}$ we have

$$\begin{aligned} \bar{i}_{L(1)} &= nFk_dA[Cr(bipy)_3^{3+}] - tk_1\bar{i}_{L(1)} \\ \bar{i}_{L(1)} &= nFk_d[Cr(bipy)_3^{3+}]/(1 + tk_1) \end{aligned} \quad (8)$$

Equation 8 has the same form as that of a normal diffusion-controlled limiting current divided by $1 + tk_1$ and is qualitatively consistent with all data reported here since $\bar{i}_{L(1)}$ is a function only of $[Cr(bipy)_3^{3+}]$, temperature (k_1), and the drop time. The quantitative treatment of the data in terms of this equation is discussed later.

Homogeneous Kinetics of the Dissociation of $Cr(bipy)_3^{3+}$.—Reactions 2 and 3 represent the catalysis of the dissociation of $Cr(bipy)_3^{3+}$ where the rate-determining step is the dissociation of $Cr(bipy)_3^{2+}$. The rate law for the homogeneous reaction may be derived by a method analogous to that used for eq. 7 but without the diffusion term. The result is $d[Cr(bipy)_3^{3+}]/dt = -k_1[Cr(bipy)_3^{2+}]$ which on integration gives

$$[Cr(bipy)_3^{3+}]_{(t=0)} - [Cr(bipy)_3^{3+}]_{(t)} = k_1[Cr(bipy)_3^{2+}]t \quad (9)$$

suggesting a linear variation of $[Cr(bipy)_3^{3+}]$ with time, with a slope of $k_1[Cr(bipy)_3^{2+}]$.

The concentration of $Cr(bipy)_3^{2+}$ added was determined from the limiting current of the anodic wave at $E_{1/2} = -0.52$ v. Since the limiting currents are linear functions of concentrations we have $i_{L(1)} = k[Cr(bipy)_3^{3+}]$ and $i_{anodic} = k'[Cr(bipy)_3^{2+}]$. Substituting these relationships into eq. 9 gives

$$i_{L(1)(t=0)} - i_{L(1)(t)} = k_1ki_{anodic}t/k' \quad (10)$$

The ratio $k/k' = 1.28/1.52$, where 1.28 and 1.52 are the diffusion current constants, I, for $Cr(bipy)_3^{3+}$ and $Cr(bipy)_3^{2+}$, respectively. These values of I were measured at 26°, and the assumption made in using the ratio at other temperatures is that the temperature coefficient of the diffusion coefficient, which is included in I, is the same for both species. Kinetic results were obtained from the slope of plots of $i_{L(1)(t)(0.65v.)}$ *vs.* time where the slope $= k_1ki_{anodic}/k'$.

Typical data are shown in Figure 6 for three different concentrations of $Cr(bipy)_3^{2+}$. The predicted linear function is obeyed well, showing the independence of the dissociation rate on $Cr(bipy)_3^{3+}$. The limiting

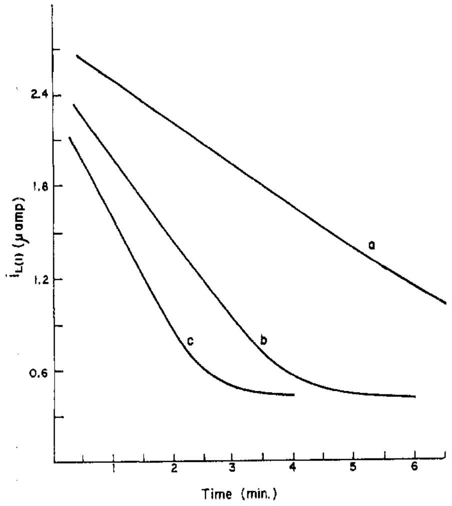

Figure 6.—Diffusion current of $Cr(bipy)_3^{3+}$ ($i_{L(1)}$) with time at −0.65 v. and 1°: $[Cr(bipy)_3^{2+}] = 0.124$ mM (a), 0.193 mM (b), 0.293 mM (c).

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(10) R. Brdicka and K. Wiesner, *Collection Czech. Chem. Commun.*, **12**, 39 (1947).

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

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

value of $i_{L(1)}$ at the completion of the reaction is that of the residual current of the supporting electrolyte. The independence of k_1 on $Cr(bipy)_3^{3+}$ and pH is shown in Table I, where each value is an average of at least two experiments. The linear, first-order dependence of the rate on $[Cr(bipy)_3^{2+}]$ is shown in Figure 7 as a plot of $\Delta i_{L(1)}/\Delta t$ *vs.* the anodic limiting current of $Cr(bipy)_3^{2+}$. The value of k_1 calculated from these data is 0.014 ± 0.002 sec.$^{-1}$ at 1°.

TABLE I

KINETIC RESULTS FOR THE HOMOGENEOUS DISSOCIATION OF $Cr(bipy)_3^{3+}$ AT 1 ± 0.5°[a]

$[Cr(bipy)_3^{2+}]$, mM	[Cr-[bipy)$_3^{3+}]_{t=0}$, mM	pH	k_1, sec.$^{-1}$
0.225	0.237	5.4	0.012
0.201	0.433	5.4	0.014
0.250	0.500	5.4	0.014
0.252	0.920	5.4	0.014
0.258	1.00	5.4	0.013
0.275	1.57	5.4	0.013
0.216	1.85	5.4	0.013
0.337	2.77	5.4	0.013
0.111	0.790	1.5	0.014
0.584	0.825	2.1	0.014
0.558	0.734	2.8	0.014
0.657	0.755	3.6	0.013
0.550	0.830	4.6	0.012
0.218	0.800	7.2	0.015
0.167	0.664	9.2	0.015

[a] 0.5 M NaCl saturated with bipyridine at pH 5.4.

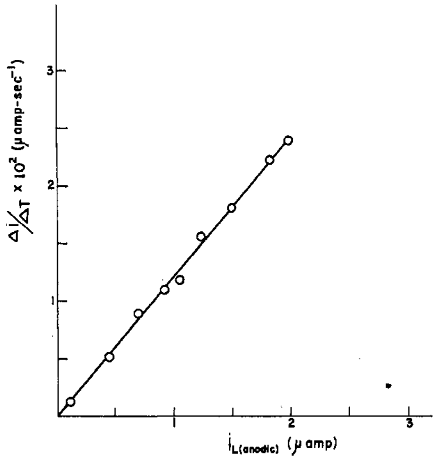

Figure 7.—Dependence of the rate of dissociation of $Cr(bipy)_3^{3+}$ on $[Cr(bipy)_3^{2+}]$.

The values of k_1 as a function of temperature are 0.023 (5°), 0.051 (10°), 0.094 (15°), 0.18 (20°), and 0.38 (25°), where each value is an average of at least three determinations reproducible to about 10%. The activation energy for reaction 2 is thus 22.6 ± 0.5 kcal., which is close to values reported for similar systems, $Co(phen)_3^{2+}$ (21 kcal.),[13] $Ni(bipy)_3^{2+}$ (21.8 kcal.),[14] and $Fe(phen)_3^{2+}$ (26 kcal.).[15] At 25° the experimental value of 0.38 sec.$^{-1}$ is in excellent agreement with the value measured by a direct method.[11]

Chemical Oxidation of $Cr(bipy)_3^{2+}$.—The chemical oxidation of $Cr(bipy)_3^{2+}$ by $Co(bipy)_3^{3+}$ and I_2 was studied by adding a solution of the oxidant to a solution of $Cr(bipy)_3^{2+}$, and the results are presented in Table II as a ratio, $i_{L(1)}/i_{L(2)}$. For solutions containing only $Cr(bipy)_3^{3+}$ this ratio is about 0.5 to 0.7 at 26°; thus an experimental ratio of this magnitude for an oxidized solution is taken to indicate that the major product of the oxidation is $Cr(bipy)_3^{3+}$, and any ratio substantially less than this indicates some $Cr(bipy)_2(H_2O)_2^{3+}$ as an oxidation product.

TABLE II

CHEMICAL OXIDATION OF $Cr(bipy)_3^{2+}$

$[Cr(bipy)_3^{2+}]$, mM[a]	Oxidant[b]	pH[c]	Temp., °C.[d]	$i_{L(1)}/i_{L(2)}$[e]
1.5	$Co(bipy)_3^{3+}$	2.5	26	0
1.5	$Co(bipy)_3^{3+}$	5.4	26	0
1.5	$Co(bipy)_3^{3+}$	10.0	26	0
1.5	$Co(bipy)_3^{3+}$	5.4	5	0.25
$Cr(bipy)_3(ClO_4)_2$ suspension	$Co(bipy)_3^{3+}$	4.5	26	0.65
$Cr(bipy)_3(ClO_4)_2$ suspension	I_2	2.1	26	0.47
1.5	I_2	4.8	26	0
1.5	$Co(bipy)_3(ClO_4)_3$ suspension	4.2	26	0.49

[a] All experiments in 0.5 M NaCl saturated with bipyridine at pH 5. [b] In all experiments except for the one with a suspension of $Co(bipy)_3(ClO_4)_3$ the oxidant was approximately 1 mM solution added to a stirred solution of $Cr(bipy)_3^{2+}$. [c] pH during or just after the oxidation. [d] Temperature during the oxidation. [e] All polarograms were measured at pH 2 and 26°. A value of the ratio = 0 indicates that no −0.49 wave was observed.

Oxidation of $Cr(bipy)_3^{2+}$ at low temperatures by $Co(bipy)_3^{3+}$ is seen to favor formation of $Cr(bipy)_3^{3+}$, although even at 5° about half of the oxidation product is still $Cr(bipy)_2(H_2O)_2^{3+}$. At higher temperatures essentially all of the product is in the latter form. The formation of $Cr(bipy)_3^{3+}$ as an isolable species is satisfactory only when a suspension of $Cr(bipy)_3(ClO_4)_2$ is oxidized. It may be seen from Table II and from the method of preparation of $Cr(bipy)_3(ClO_4)_3$ in the Experimental section that the oxidation product is independent of the oxidizing agent used. Thus, $Co(bipy)_3^{3+}$, I_2, and O_2 all produce only the bis species from solutions, but all give tris species from suspensions. From a suspension of $Cr(bipy)_3(ClO_4)_2$ the concentration of catalyst ion is probably too small to result in the dissociation of the tris product.

The oxidation[2,3] of $Cr(bipy)_3^{2+}$ by $Co(NH_3)_6^{3+}$ may now be understood in the same terms. The reaction probably proceeds first to $Cr(bipy)_3^{3+}$, which then dissociates in the presence of the unreacted $Cr(bipy)_3^{2+}$, although the dissociation of $Cr(bipy)_3^{2+}$ followed by oxidation of $Cr(bipy)_2(H_2O)_2^{2+}$ is not ruled out by these data.

Discussion

A comparison of our results with the polarographic results of ref. 4 shows two major differences. The

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[13] R. G. Wilkins and P. Ellis, *J. Chem. Soc.*, 299 (1959).

[14] F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Am. Chem. Soc.*, **75**, 5102 (1953).

[15] J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 736 (1950).

reduction of $Cr(bipy)_3^{3+}$ was observed by Vlcek to occur in three one-electron steps of equal heights at −0.36, −0.73, and −1.38 v. At 1° we obtain three waves of equal height at −0.51, −0.90, and −1.3 v. Qualitatively the two sets of polarograms are similar; thus the first wave is reversible, the second is discontinuous, and the third is irreversible. At higher temperature we observe a fourth wave at −0.72 v. The general similarity of the two sets of results and the development of the foregoing reaction mechanism lead to the conclusion that the waves at −0.51, −0.90, and −1.3 v. of this investigation correspond to the −0.36, −0.73, and −1.38 v. waves of ref. 4. The wave we observe at −0.72 v. is therefore considered to be an anomalous one and the failure of Vlcek to observe it is discussed below. The difference in potentials between the two sets of results is difficult to explain.

The validity of the kinetic results for the homogeneous dissociation of $Cr(bipy)_3^{3+}$ depends to an extent on the wave assignments made for the polarograms, and the wave assignments, in turn, depend upon the validity of the mechanism postulated for the electrode reactions. The unifying feature of the data is its self-consistency and the excellent agreement of the value of k_1 measured herein with the previous value measured directly. This agreement strongly supports the postulated homogeneous dissociation mechanism and strongly suggests that the same mechanism accounts for the anomalous polarographic wave, although the latter conclusion cannot be accepted without reservation.

Equation 8 may be rearranged to give

$$k_1 = (\bar{\imath}_{L(t)} - \bar{\imath}_{L(1)})/t\bar{\imath}_{L(1)} \tag{11}$$

where $\bar{\imath}_{L(1)} = nfk_d[Cr(bipy)_3^{3+}] = \bar{\imath}_{L(1)} + \bar{\imath}_{L(2)}$. The ratio of currents in eq. 11 is a function of temperature owing to the effect of temperature on both the value of k_1 and the diffusion coefficient governing $\bar{\imath}_{L(t)}$. The effect of temperature on diffusion coefficients may be corrected for by the value $d \ln i/dt = 1.6\%$ deg.$^{-1}$ obtained previously. In Figure 8 k_1 obtained from temperature-dependence data is plotted against $\bar{\imath}_{L(t)} - \bar{\imath}_{L(1)}/\bar{\imath}_{L(1)}$ where $\bar{\imath}_{L(t)}$ is the experimental value at 25° and $i_{L(1)}$ is the value observed at the temperature corresponding to k_1 but corrected to 25° for the temperature effect on diffusion.

The predicted linear relationship is observed between 1 and 30°. The deviation from linearity above this temperature is possibly due to an increased importance of the reverse of reactions 2 and 3, or it may be related to the approximate nature of the diffusion term in eq. 7. The value of t calculated from the linear portion of this curve is 2.1 sec. compared with an experimental value of 3.6 sec. for the capillary used in this experiment. A more rigorous derivation and a study of the current–time relationship over the lifetime of the mercury drop are probably necessary to clarify the electrode mechanism.

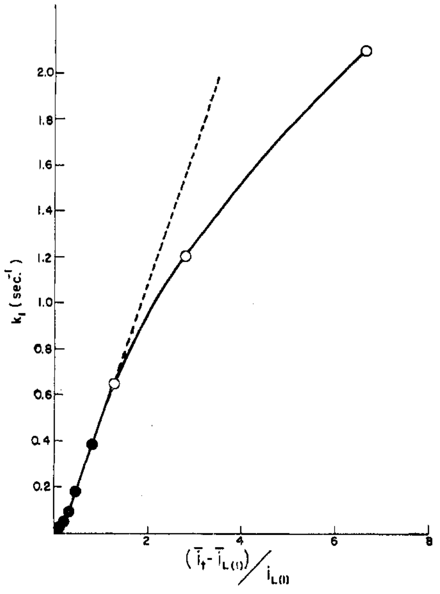

Figure 8.—Relationship of the relative first and second limiting currents of $Cr(bipy)_3^{3+}$ to the rate of dissociation of $Cr(bipy)_3^{2+}$.

The absence of the anomalous second wave in the results of ref. 4 may be due to three factors. This wave has been shown to be obscured by higher pH (>6), by low temperatures, and by a short drop time. A fourth wave at low pH is referred to in ref. 4, but it is not clear at what potential this occurs. The effect of drop time was studied in a preliminary experiment at 26° by varying t (and also m, incidentally) by varying the length of the mercury capillary. By rearranging eq. 11 we have $t = (\bar{\imath}_{L(t)} - L\bar{\imath}_{(1)})/k_1\bar{\imath}_{L(1)}$. A plot of t *vs.* the current ratio was linear as expected, with a value of $k_1 = 0.1$ sec.$^{-1}$ calculated from the slope. Using this value, and $t = 4.68$ sec., the ratio $i_{L(1)}/i_{L(2)}$ was calculated to be 0.5 at 26°, in good agreement with the data of Figure 1. Using $t = 2$ sec. at 20° (the temperature used in ref. 4) the ratio is 0.9. Under these conditions the anomalous wave would be barely discernible. Unfortunately, the details of pH and drop time are not reported in ref. 4 so the foregoing calculations are purely speculative.

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