A Polarographic Study of the Bis(2,2',2''-Terpyridine) Chromium(II) Cation

Michael C. Hughes and Daniel J. Macero

The polarographic behavior of $Cr(terpy)_2^{2+}$ was studied in aqueous solution, using AC and DC techniques. Three waves were observed. The first wave was due to a diffusion controlled one-electron oxidation, the second to a diffusion controlled one-electron reduction. The third wave was not studied. The polarographic behavior of $Cr(terpy)_2^{3+}$ and $Cr(bipy)_3^{2+}$ were also reported briefly and compared with the behavior of $Cr(terpy)_2^{2+}$.

Introduction

Complexes of the tridentate ligand 2,2',2''-terpyridine (terpy) and related ligands have been reported for most of the divalent ions of the first row transition metals.[1-5]

Comparatively little work has been reported on complexes of chromium(II). Farina and Wilkins[6] have reported the preparation and visible spectrum of $Cr(terpy)_2^{2+}$, and Herzog and Aul[7] have reported the preparation and magnetic moment of $Cr(terpy)_2I_2 \cdot H_2O$. Vlcek[8] reported the DC polarographic reduction of the related tris(bipyridine) chromium(II) cation and the oxidation of $Cr(bipy)_3^{2+}$ generated by the Kalousek commutator. Baker and DevMehta[9] also reported the DC polarography of tris(bipyridine) chromium(II) and the AC polarography of the same compound has been briefly reported by Kisova and Tvaruzek.[10] Both of these studies, however, were concerned primarily with the reduction of the chromium(III) complexes of bipyridine. The present study of the voltammetric behavior of the bis(terpyridine) chromium(II) cation was undertaken in conjunction with the recent studies of the bis(terpyridine) iron(II) cation[11] and the bis(terpyridine) cobalt(II) cation[12] done in this laboratory.

Experimental Section

General. The ligand, 2,2',2''-terpyridine, was obtained from G. Frederick Smith Co. Tetramethylammonium chloride (TMAC) was of polarographic grade and obtained from Southwestern Analytical Chemical Co. Both were used as received. All other chemicals were reagent grade. High purity nitrogen was washed first with acidic chromous chloride solution and then with alcoholic KOH solution before use. Solutions of chromium(II) chloride were prepared by constant potential electrolysis of chromium(III) choloride at a stirred mercury pool in acidic 0.1 *M* KCl. The chromous chloride solutions were kept under nitrogen at a constant reducing potential of −1.1 volts *vs.* S.C.E. The chromium(II) solutions were analyzed by adding to excess deaerated standard ceric ammonium sulfate and back titrating with standard ferrous ammonium sulfate. The titration was followed potentiometrically. Visible spectra were also run on the solutions. From these and the value of 5.1 for the molar absorptivity of $CrCl_2$ at 14×10^3 cm^{-1} [13] the concentration of the chromous solutions was calculated. These calculations agreed to within 1-2% of the values obtained by the titrimetric method. In some of the solutions an absorption band was also observed at 24.5×10^3 cm^{-1}. The intensity of this band relative to the band at 14.0×10^3 cm^{-1} varied from solution to solution and its presence was ascribed to small amounts of chromium(III) in the solutions.[14]

Bis(terpyridine) chromium(II) chloride solutions were prepared *in situ* by the addition of chromous chloride solution to a deaerated solution of terpyridine in 0.1 *M* TMAC. The TMAC was dissolved in 50% ethanol to facilitate solution of both the terpyridine and the complex. All chromous solutions were very sensitive to air oxidation and therefore all preparations and manipulations were carried out under a nitrogen atmosphere.

Bis(terpyridine) chromium(III) perchlorate was prepared after a procedure described by Baker and DecMehta.[9] One half gram of terpyridine and 1 gram of $NaClO_4$ were dissolved in 50 ml of distilled water. The solution was deaerated for one hour and 10 ml of 0.1 *M* Cr^{2+} added. After several minutes a black precipitate of $Cr(terpy)_2(ClO_4)_2$ formed, which was oxi-

(1) G. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1649 (1937).
(2) R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 341 (1962).
(3) W. A. Baker, Jr. and J. Judge, *Inorg. Chim. Acta*, 1, 68 (1967).
(4) W. A. Baker, Jr. and J. Judge, *ibid.*, 1, 239 (1967).
(5) W. A. Baker, Jr., J. Judge, G. Intille, and W. Reiff, *J. Inorg. Nucl. Chem.*, 29, 1711 (1967).
(6) R. Farina and R. G. Wilkins, *Inorg. Chem.*, 7, 515 (1968).
(7) S. Herzog and H. Aul, *Z. Chem.*, 6, 382 (1966).
(8) A. A. Vlček, *Nature*, 189, 393 (1961).
(9) B. Baker and B. DevMehta, *Inorg. Chem.*, 4, 848 (1965).
(10) L. Kisova and P. Tvaruzek, *Coll. Czech. Chem. Comm.*, 30, 3565 (1965).
(11) F. V. Lovecchio, S. J. Pace, and D. J. Macero, *Inorg. Chim. Acta*, 3, 94 (1969).
(12) D. J. Macero, F. V. Lovecchio, and S. J. Pace, *Inorg. Chim. Acta*, 3, 65 (1969).

(13) J. P. Fackler and D. G. Holah, *Inorg. Chem.*, 4, 954 (1965).
(14) R. L. Pecsok and W. P. Schaeffer, *J. Am. Chem. Soc.*, 83, 62 (1961).

dized to the yellow-orange bis(terpyridine) chromium(III) perchlorate by bubbling with chlorine gas for approximately one hour. The precipitate was filtered, washed with an ethanol water mixture, and dried to constant weight under vacuum. Calculated for $Cr(terpy)_2(ClO_4)_3 \cdot 2H_2O$: C, 42.26; H, 3.05; N, 9.85. Found: C, 42.36; H, 2.97; N, 9.87.

Absorption Spectra. Solutions were prepared which were identical, except for concentration, to those used for the polarographic runs. Chromous chloride solution was added to excess terpyridine or bipyridine in $0.1 M$ TMAC in 50% ethanol. Bis(terpyridine) chromium(III) perchlorate was dissolved in excess terpyridine in the same background. The principle absorption peaks in the region 700-350 nm are listed. Molar absorptivities are given in parentheses. The values for the complexes of divalent chromium complexes of terpyridine and bipyridine compare favorably with literature values.[6,15]

$Cr(terpy)_2^{2+}$: 553 nm (2.1×10^3); 504 nm (4.1×10^3); 406 nm (5.5×10^3).

$Cr(terpy)_2^{3+}$: 477 nm (1.5×10^3); 450 nm (2.5×10^3); 436 nm (2.2×10^3).

$Cr(bipy)_3^{2+}$: 566 nm (3.9×10^3); 475 nm (3.7×10^3).

Apparatus. Both the DC and AC polarograms were obtained with an instrument assembled from Philbrick Researches solid state operational amplifiers and other standard electronic components. A Moseley Model 7001A X-Y recorder was used to obtain permanent DC and AC polarographic records. A Beckman Zeromatic pH meter was used to determine pH values. Absorption spectra were taken with a Beckman Model DB recording spectrophotometer. A conventional thermostated polarographic H-cell was used for all measurements. A saturated potassium chloride calomel electrode was used as a reference electrode for the DC and AC polarographic measurements. The temperature for the current *vs.* concentration and current *vs.* column height studies was maintained at $25.0 \pm 0.1°C$. Other runs were maintained at $25 \pm 1°C$. All polarographic runs employed a dropping mercury electrode whose capillary constants were $t = 3.63$ sec, $m = 1.95$ mg sec^{-1} in $0.1 M$ TMAC in 50% ethanol at 0 volts *vs.* S.C.E. at a column height of 60.0 cm.

Results

Polarograms of the bis(terpyridine) chromium(II) cation in excess terpyridine in $0.1 M$ TMAC at pH 7.1 (Figure 1) show an oxidation wave with $E_{1/2}$ of —0.285 volt *vs.* S.C.E. and a reduction wave with $E_{1/2}$ of —0.695 volt *vs.* S.C.E. A third wave is observed in the region of —1.0 volt *vs.* S.C.E. This wave is discontinuous and was not investigated extensively.

The oxidation wave and the first reduction wave were both determined to be faradaic in nature and diffusion controlled. This was indicated by the linear variation of the limiting current with the square root of the mercury column height (Figure 2). In addition,

(15) P. M. Lutz, Ph. D. Dissertation, Syracuse University (1970).

the diffusion current was found to be directly proportional to the concentration of chromium terpyridine complex over a range of from 0.5 to 4.0 mM (Figure 3).
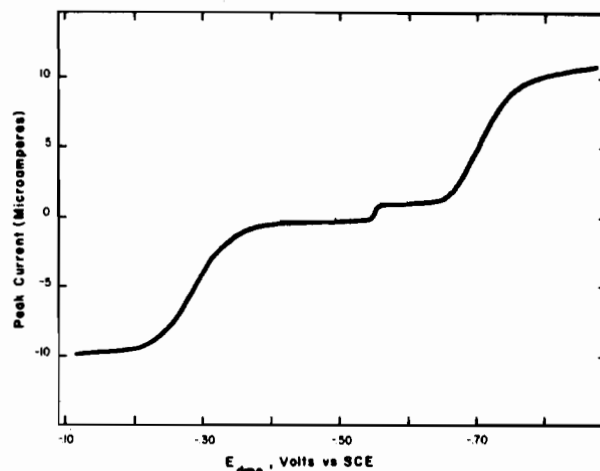

Figure 1. Maximum current DC polarogram of 3.17 mM $Cr(terpy)_2^{2+}$.

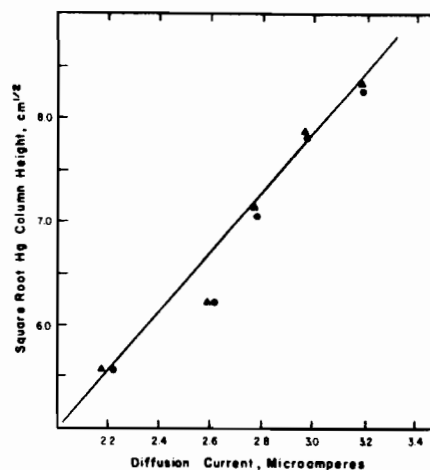Figure 2. Plot of current *vs.* Mercury column height for first (oxidation) wave and second (reduction) wave of 1.92 mM $Cr(terpy)_2^{2+}$. ● - oxidation wave; ▲ - reduction wave.
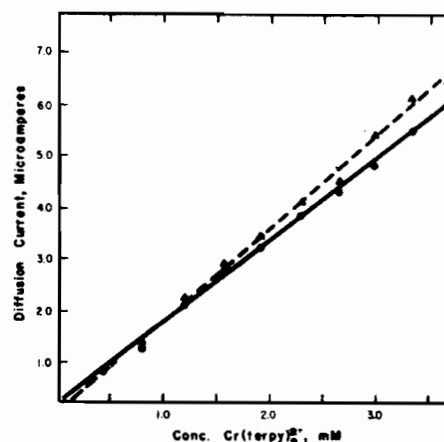

Figure 3. Plot of current *vs.* concentration for $Cr(terpy)_2^{2+}$. (● ——) first (oxidation) wave; (▲ – – –) second (reduction) wave.

A polarogram of $Cr(terpy)_2^{2+}$ was also run without any excess ligand. The diffusion plateau of the second reduction wave, in this case, extended to -1.9 v vs. S.C.E., nearly 0.6 v more negative than the reduction potential of free terpyridine in the same supporting electrolyte. This would seem to indicate that the complex undergoes the various electron transfer processes without the loss of complexed terpyridine.
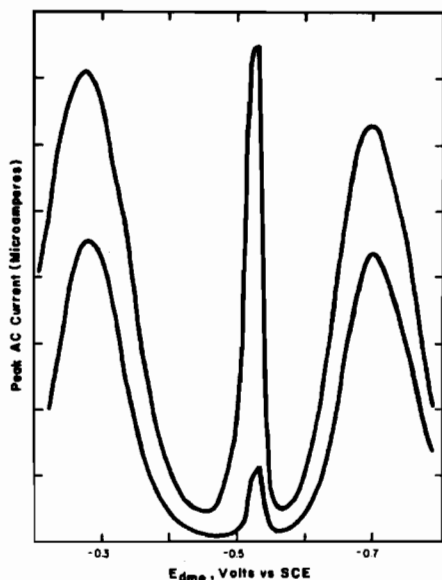

Figure 4. Peak-current In-Phase AC polarograms of 3.17 mM $Cr(terpy)_2^{2+}$. Ordinate = 0.5 microamperes per division. Upper curve, frequency = 100 Hz; Lower curve, frequency = 20 Hz.

The pre-wave, which occurs in the potential region -0.55 to -0.65 volt vs. S.C.E., apparently originates from an adsorption-desorption process coupled with a faradaic process, both processes involving the complex. Phase selective AC polarographic measurements indicate that the pre-wave is essentially non-faradaic in nature. In Figure 4 is shown the frequency dependence of the in-phase current of the pre-wave as well as that of the two main waves. It is seen that the current due to the pre-wave increases much more rapidly with increasing frequency than that of either of the two main waves. Figure 5 shows the in-phase and the 90° out-of-phase AC polarograms for the same frequency. In the latter, or quadrature component polarogram, the current of the other two waves is decreased. In both cases, the pre-wave behavior is typical of a non-faradaic process,[16] and is similar to that previously reported for bis(terpyridine) iron(II),[11] and bis(terpyridine) cobalt(II).[12] Quadrature component AC polarograms of solutions of free terpyridine in 0.1 M TMAC in 50% ethanol show no polarographic activity in the region of the pre-wave.

While the frequency and phase angle dependence of the AC polarograms of the pre-wave indicate an essentially non-faradaic process, other characteristics of the wave seem to indicate that some faradaic pro-

cess contributes to the pre-wave and that this process is distinct from the one causing the main reduction wave with $E_{1/2}$ of -0.695 volt vs. S.C.E. The exact nature of the processes contributing to the pre-wave are uncertain. It is possible that the mechanism involves product adsorption. However, this is somewhat speculative at this time. Further studies are currently underway with bis(terpyridine) chromium(II) and similar complexes in an effort to determine the mechanism.[17]
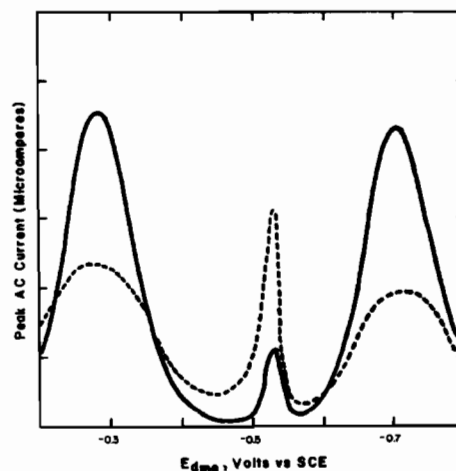

Figure 5. Peak current In-Phase (————) and Quadrature component (------) AC polarograms of 3.17 mM $Cr(terpy)_2^{2+}$. Frequency = 20 Hz. Ordinate = 0.5 microamperes per division.
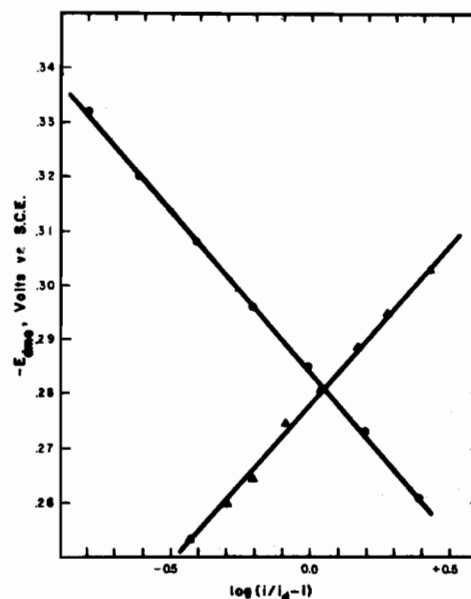

Figure 6. Plots of $\log(i/i_d-)$ vs. E_{dme} for the first (oxidation) wave (● ——) and the second (reduction) wave (▲ ——) of $Cr(terpy)_2^{2+}$.

The oxidation wave, $E_{1/2} = -0.285$ v vs. S.C.E., was determined to be due to the oxidation of $Cr(terpy)_2^{2+}$

(16) B. Breyer and S. Hacobian, Aust. J. Sci. Res. A5, 500 (1952).

(17) F. V. Lovecchio, M. C. Hughes, D. J. Macero, unpublished results.

Hughes, Macero | Polarography Terpyridine Chromium

to $Cr(terpy)_2^{3+}$. Comparison with the half-wave potential of −0.280 v vs. S.C.E. obtained for the first reduction wave of $Cr(terpy)_2^{3+}$ indicates that this electrode process is reversible. Plots of the electrode potential vs. $\log[i/(i_d-i)]$ for both the oxidation wave of $Cr(terpy)_2^{2+}$ and the first reduction wave of $Cr(terpy)_2^{3+}$ are shown in Figure 6. Both plots are linear and show a slope of 57 mV, indicating a one electron transfer for each. Finally, the low frequency AC polarograms of the oxidation wave of $Cr(terpy)_2^{2+}$ are symmetrical about a peak potential of −0.285 v vs. S.C.E. and have a half-peak width of 97-100 mV which is typical behavior observed for a reversible, one-electron change.

The DC current values for the first reduction wave with $E_{1/2}$ of −0.695 volt vs. S.C.E. are slightly higher when measured from the residual current than those for the corresponding oxidation waves. For reasons previously mentioned, the current due to the pre-wave was subtracted from the total current measured for the first reduction wave. The net DC diffusion current measured this way was now essentially the same as the current of the corresponding oxidation wave. A plot of E vs. $\log[i/(i_d-i)]$ for the first reduction wave is linear except for a small positive deviation near the foot of the wave, and has a slope of 64 mV, indicating a one electron change assuming the electrode reaction is reversible. The deviation from linearity near the foot of the wav was believed to be caused by the presence of the pre-wave. Evidence that the electron transfer for this process is reversible is obtained from AC polarograms of the reduction wave. At low AC frequencies these exhibit a symmetrical shape, a half-peak width of 97-100 mV, and very nearly the same AC current as the oxidation wave. On the basis of this evidence, the first reduction wave at −0.695 v vs. S.C.E. is taken to be due to the reversible reduction of $Cr(terpy)_2^{2+}$ to $Cr(terpy)_2^{1+}$.

The second reduction wave which occurs at a potential of approximately −1.0 v vs. S.C.E. is discontinuous. The limiting current appears to be approximately equal in value to that of the first reduction wave.

Polarograms were run of Cr^{2+} in a ten-fold excess of bipyridine dissolved in the same background as used in the studies of $Cr(terpy)_2^{2+}$. In neutral solutions the results obtained were similar to those obtained by Vlcek[8] for $Cr(bipy)_3^{3+}$. Three waves were observed, an oxidation wave at −0.38 v vs. S.C.E., and two reduction waves, at −0.89 v vs. S.C.E. and −1.3 volt vs. S.C.E. A pre-wave occured at −0.72 volt vs. S.C.E. which was shown by AC polarography to have the same characteristics as the pre-wave observed for the terpyridine complex. Each of the three waves of $Cr(bipy)_3^{2+}$ had approximately the same height, and the reduction wave at −1.3 v was discontinuous.

Vlcek[18] has noted the influence of substitution on the ligand upon the reduction potentials of both the ligand and the metal complex. In particular, substitution of aromatic groups upon the ligand has the effect of causing the reduction potential of the free ligand to become more positive, while the reduction potential of the complex also becomes more positive, but the shift is smaller for the complex. Bipyridine is not observed to reduce at all in the region accessible to the DME in the supporting electrolyte used in these studies, but terpyridine shows several reduction waves, the first at −1.35 v vs. S.C.E. A similar, but smaller shift of about plus 95 mV is noted in going from the $Cr^{II}-Cr^{III}$ bipyridine couple to the $Cr^{II}-Cr^{III}$ terpyridine couple. It is interesting to note that the same positive shift is observed for the $Cr^{II}-Cr^{I}$ couple with the two ligands, but that the shift is considerably larger, being approximately 200 mV.

(18) A. Vlcek in « Progress in Inorganic Chemistry », Vol. 5, F. Albert Cotton, Ed., Interscience, New York, N. Y. (1963), pp. 353-358.