*Contribution from the Department of Chemistry,
Syracuse University, Syracuse, N.Y., 13210, U.S.A.*

Polarographic Evidence for the Formation of a Cobalt(I) Complex with Terpyridine

D. J. Macero, F. V. Lovecchio, and S. J. Pace

Received November 16, 1968

AC and DC polarographic studies of the reduction of a divalent cobalt complex containing the ligand 2,2′,2″-terpyridine were undertaken, and evidence is given for the existence of a stable univalent cobalt complex ion in aqueous solution. Diffusion controlled waves were obtained for the $Co(terpy)_2^{2+}$ *species in boric acid buffer [pH 7.5] with and without excess ligand. A small pre-wave which is attributed to adsorption is observed. The heterogeneous rate constant and transfer coefficient are evaluated for the main wave.*

Introduction

Stable six co-ordinate complexes of trivalent cobalt involving ligands with nitrogen donor atoms are well known and have been extensively studied. The corresponding cobalt(II) complexes, on the other hand, are less numerous. One such type of divalent cobalt complex contains the tridentate ligand, 2,2′2″-terpyridine [terpy].[1] Hogg and Wilkins[2] report the preparation of cobalt(II) terpyridyl complexes and have characterized the magnetic and spectral properties of these compounds. Baker, *et.al.*[3,4,5] have also prepared and studied a number of terpyridyl complexes of first row transition metals.

Waind and Martin[6] examined the polarographic behavior of tris(2,2′-dipyridine)cobalt(III) ion, $Co(dipy)_3^{3+}$, in aqueous solution and report the formation of two waves corresponding to reduction to the Co^{II} and Co^{I} complex, respectively. Maki and co-workers[7] claim the preparation of the monovalent cobalt complex, $Co(phen)_3ClO_4$, in ethanol solution at –5°C. The similarity of the terpyridine ligand to bipyridine and phenanthroline and the possibility of generating a monovalent cobalt terpyridyl complex prompted us to study the polarographic behavior of the cobalt(II) terpyridine system

Experimental Section

Chemicals. With the exception of the cobalt terpyridyl complex all chemicals were of reagent grade and used without further purification. The $Co(terpy)_2(ClO_4)_2$ was synthesized by J. Judge and donated by W. A. Baker, Jr. The cobalt complex was stored in a vacuum dessicator prior to dissolution in a boric acid-sodium borate buffer of pH 7.5. The terpyridine was used as received from the G. Frederick Smith Chemical Company. Twenty percent by volume of methanol was added to the solutions to increase the solubility of terpyridine. The concentrations of the $Co(terpy)_2^{2+}$ solutions were checked by measuring the absorbance at 505 mμ.[8]

Apparatus. The DC polarograms were obtained with an Indiana Instrument and Chemical Corp. *Controlled Potential and Derivative Voltammeter,* Model ORNL-1988A. AC polarograms were obtained with an instrument assembled form Philbrick Researches solid state operational amplifiers and standard electronic components. The AC polarograph was modified after instruments described by Hayes and Reilley[9] and Smith.[10] A Moseley Model 7001 X–Y recorder was used to obtain permanent DC and AC polarographic records. A Beckman Model G pH meter was used to determine pH values. Absorption spectra were taken with a Beckman Model DB recording spectrophotometer. A conventional thermostated polarographic cell was used for all measurements. A saturated sodium chloride calomel electrode was used as the reference electrode for the DC polarographic runs and a saturated potassium chloride, silver-silver chloride reference electrode for the AC runs. The temperature was maintained constant at 25.0±0.1°C.

Results and Discussion

Polarograms of millimolar concentrations of the bis(2,2′,2″-terpyridine) cobalt(II) cation in boric acid buffer in excess terpyridine were taken and a typical example is shown in Figure 1. A small pre-wave occurs at about –0.8 volt *vs.* SCE prior to a larger well-defined wave at –0.983 volt *vs.* SCE. A polarogram of the terpyridine ligand alone in boric acid buffer showed no appreciable reduction until a voltage of –1.2 volts *vs.* SCE was reached.

The pre-wave was judged to be non-faradaic in

---

(1) G. Morgan and F. 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. M. Intille, and W. M. Reiff, *J. Inorg. Nucl. Chem., 29,* 1711 (1967).
(6) G. Waind and B. Martin, *J. Inorg. Nucl. Chem., 8,* 551 (1958).
(7) N. Maki, M. Yamagami, and H. Itatani, *J. Am. Chem. Soc., 86,* 514 (1964).
(8) M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed., 15,* 74 (1943).
(9) T. W. Hayes and C. N. Reilley, *Anal. Chem., 37,* 1322 (1965).
(10) D. E. Smith, *Anal. Chem., 35,* 1811 (1963).

nature after consideration of AC polarograms taken on the same system at frequencies of 20 and 100 Hz.

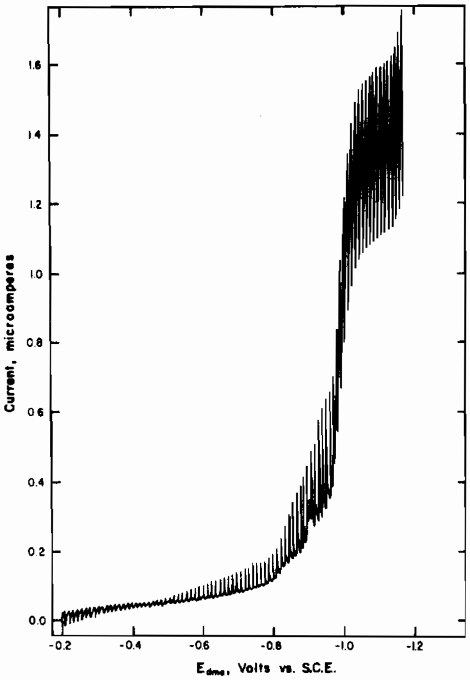

Figure 1. DC polarogram of 0.5 m*M* Co(terpy)$_2^{2+}$ in boric acid-sodium borate buffer +20% methanol, pH=7.5. 2.0 m*M* excess terpyridine.

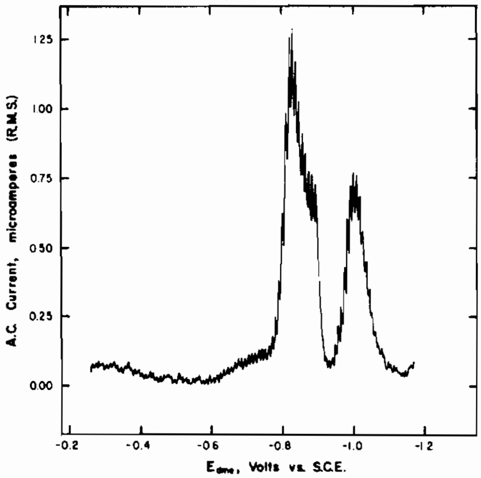

Figure 2. Phase selective AC polarogram of 0.5 m*M* Co(terpy)$_2^{2+}$ in borate buffer, pH=7.5. 2.0 m*M* excess terpyridine. Applied potential: 20 Hz, 8 mv peak-to-peak a.c. signal, 50 mv min^{-1} d.c. scan rate.

A representative AC polarogram of the cobalt terpyridine complex, shown in Figure 2, exhibits two peaks; one at the potential of the pre-wave, the other at the potential of the main wave. The first AC wave, *i.e.* the DC pre-wave, has the characteristics of an adsorption-desorption process.[11] Supporting evidence for this conclusion is also obtained from AC polarograms of terpyridine in boric acid buffer. These show an AC wave with a peak potential of –0.8 v *vs.* SCE, whereas the DC polarograms for this same system show no polarographic activity until quite negative potentials are reached. The non-faradaic nature of the pre-wave is further substantiated by current-time curves obtained on individual drops in the potential region of the pre-wave. The shapes of these curves are typical of charging current curves. Because of these considerations the pre-wave is excluded from any further discussion of the polarographic behavior of the cobalt(II) complex.

The main wave was ascertained to be due to a faradaic process and to be diffusion controlled with no appreciable kinetic complications. This was concluded from the linear variation of limiting current with the square root of mercury column height. This is depicted in Figure 3. A similar conclusion is reached from the invariance of AC peak current with column height for this system.

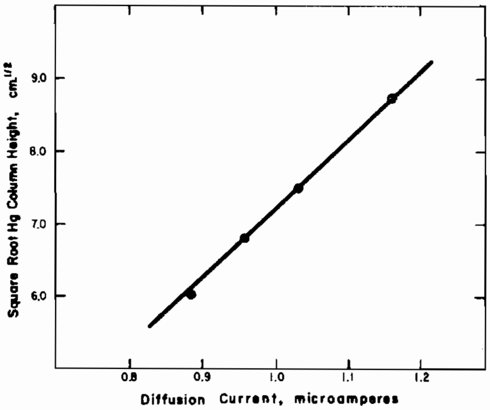

Figure 3. Dependence of the diffusion current of the cobalt complex on the mercury column height.

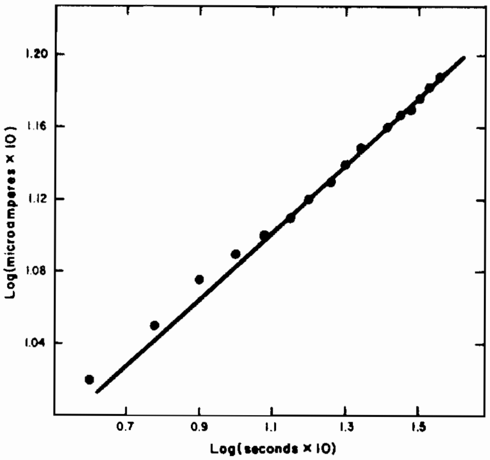

Figure 4. Log analysis of current-time curves of Co(terpy)$_2^{2+}$ on the limiting current plateau of the DC polarogram.

Further confirmation that the limiting current is diffusion controlled was obtained by examining the current-time curves taken on individual drops in the limiting current region. The second and subsequent

---

(11) B. Breyer and S. Hacobian, *Australian J. Sci. Res.*, *A5*, 500 (1952).

drops were used. These curves all exhibit a shape characteristic of a diffusion controlled process. In addition the plot of log i *vs.* log t shown in Figure 4 has a slope of 0.19 toward the end of the drop life. This value compares favorably with the theoretical value of 0.192 for a diffusion controlled current for serial drops[12] and with the experimentally determined value of 0.18 obtained at this laboratory for cadmium ion in 0.1 *M* KCl.

The diffusion current was found to be directly proportional to the concentration of the complex over the range of 0.2 to 0.5 m*M* $Co(terpy)_2^{2+}$.

Polarograms of 0.5 m*M* $Co(terpy)_2^{2+}$ were also run with no excess ligand. In this case, the diffusion current remained unchanged, and the shape of the main wave was better defined. The diffusion plateau for this system extended to −1.5 volt *vs.* SCE, a full 0.3 v more negative than the reduction potential of uncomplexed terpyridine. This would indicate that terpyridine is not liberated from the product of the electrode reaction, suggesting the possibility that the co-ordination sphere of the complex remains intact during the course of reduction.

A value for *n*, the number of electrons transferred in the faradaic process, was established in several ways. First, *n* was calculated directly from the Ilkovič

$$i_d = 607\,nCD^{1/2}m^{2/3}t^{1/6}$$

equation, where i_d is the diffusion current in microamperes; D, the diffusion coefficient in cm²/sec; C, is the concentration of electroactive species in millimoles/liter; m, the mercury flow rate in mg/sec and t is the drop time in seconds. Values for m and t were determined to be 2.3 mg/sec. and 3.2 seconds, respectively. A value for the diffusion coefficient for $Co(terpy)_2^{2+}$ was estimated by assuming it to be equal to that determined experimentally for an ion of similar charge, size and structure, *i.e.* $Fe(dipy)_3^{2+}$ which has the value 4.6×10^{-6} cm²/sec. at 25°C.[13] When these values are used along with experimental values of concentration and current a value of 0.83 is calculated for *n*. This indicates that the cobalt(II) terpyridyl complex is reduced to the monovalent species, $Co(terpy)_2^{+}$.

Second, a comparison of values for the diffusion current constant, I, which is defined as the quotient, $i_d/Cm^{2/3}t^{1/6}$, was made for a number of different ions.[14,15,16] These values are presented in Table I along with that obtained for the cobalt(II) complex in the present investigation. Clearly from this table, values of I of from 0.9 to 1.6 correspond to one electron reductions while for two electron changes one expects values of I in the range of from 2 to 3.6. The value of 1.1 determined for the reduction of $Co(terpy)_2^{2+}$ ion indicates a one electron change or that a monovalent cobalt species has been produced.

Table I. Values for the Diffusion Current Constant, I for one and two Electron Transfer.

Reaction	Background Electrolyte	I	Ref.
One electron changes			
$Fe^{III} \rightarrow Fe^{II}$	sodium citrate	0.93	14
$Fe^{III} \rightarrow Fe^{II}$	sodium tartrate, pH 4	1.11	14
$Mn^{II} \rightarrow Mn^{III}$	0.1 *M* sodium tartrate, 2.0 *M* NaOH	−0.95	15
$Ti^{IV} \rightarrow Ti^{III}$	0.1 *M* ammonium citrate, pH 6.1	1.02	15
$Cr^{III} \rightarrow Cr^{II}$	0.1 *M* NH_3, 0.1 *M* ammonium citrate, pH 8.5	1.23	15
$Cr^{III} \rightarrow Cr^{II}$	1 *M* KCN	1.55	16
Two electron changes			
$Co^{II} \rightarrow Co^{0}$	0.1 *M* NH_3, 0.1 *M* ammonium tartrate	1.88	15
$Ni^{II} \rightarrow Ni^{0}$	0.1 *M* pyridine, 0.1 *M* pyridinium chloride	2.6	15
$Co^{II} \rightarrow Co^{0}$	0.1 *M* NH_3, 0.1 *M* ammonium citrate, pH 8.5	2.43	15
$Co^{II} \rightarrow Co^{0}$	1 *M* NH_3, 1 *M* NH_4Cl	3.4	15
$Ni^{II} \rightarrow Ni^{0}$	1 *M* NH_3, 0.2 *M* NH_4Cl	3.54	15
$Co(terpy)_2^{2+}$	Boric acid-sodium borate pH 7.5	1.1	

Third, an estimate of *n* was made from the observed slope of 50 mv for the linear plot of the electrode potential, E, *vs.* the function, $\log\left(\frac{i}{i_d - i}\right)$ shown in Figure 5. This plot was made from a polarogram of 0.5 millimolar $Co(terpy)_2^{2+}$ in boric acid buffer with excess terpyridine present. Assuming the electrode reaction is reversible such a slope would correspond to a value of 1 for *n*. Again a one electron reduction is indicated. When a similar plot was made for polarograms of solutions of the cobalt complex containing no excess ligand, a least squares plot gave a slope of 57 mv. The low value of 50 mv can be attributed to the uncertainty of the points at potentials more positive than the half-wave potential because of the presence of the pre-wave. In this con-

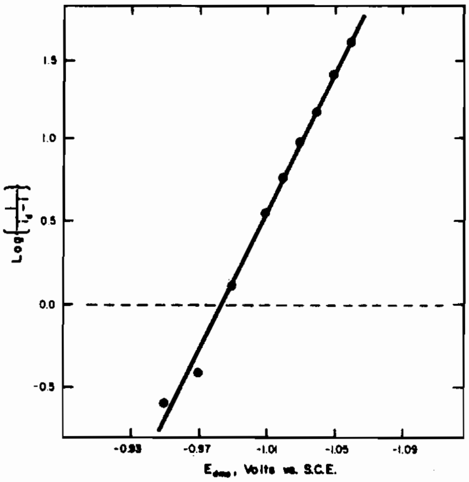

Figure 5. Plot of $\log\left(\frac{i}{i_d - i}\right)$ versus potential for the DC polarogram of Figure 1.

---

(12) J. Kuta and I. Smoler in « Progress in Polarography », Vol. 1, P. Zuman and I. M. Kolthoff, Eds., Intersicence, New York, N. Y., (1962), pp. 43-63.

(13) F. Pantini and G. Ciantelli, *J. Electroanal. Chem.*, *14*, 423 (1967).

(14) J. J. Lingane, *J. Am. Chem. Soc.*, *68*, 2448 (1946).

(15) L. Meites, « Polarographic Techniques », 2nd ed, Interscience, New York, N. Y., 1964, pp. 623-655.

(16) D. N. Hume, *J. Am. Chem. Soc.*, *65*, 1897 (1943).

nection it is noteworthy that Waind and Martin[6] report an E *vs.* $\log(\frac{i}{i_d - i})$ slope of 58 mv for the reduction step: $Co(dipy)_3^{2+} + e = Co(dipy))_3^+$ in KNO_3 solution. No mention of a pre-wave is made in their work.

Finally, consideration of the second wave in the AC polarogram (Figure 6) which corresponds to the main wave in the DC polarogram yields a value for n. This wave is symmetrical in shape which indicates that the electrode reaction is the result of a reversible, diffusion controlled process at the frequency employed. Furthermore the wave at one half the peak height has a width of 90.3 mv which agrees very well with the expected value of 90 mv for a one electron reversible reduction.[17]

A more detailed analysis of the AC polarograms, produced a value of 0.099 cm/sec for the heterogeneous rate constant, $k_{s,h}$, and a value of 0.44 for the transfer coefficient, α, at a frequency of 100 H_{wfz}. In obtaining these two parameters corrections for double layer charging current and solution IR drop were made vectorially according to the method of Smith.[17]

The moderately large value for the heterogeneous rate constant implies that the electrode reaction is quasi-reversible with no appreciable kinetic complications. In fact for DC polarography such a high rate constant is not detectable and hence the requirement that the reduction step be reversible when deducing *n* from the slope of the E *vs.* log i plot is valid. The value of 0.44 observed for the transfer coefficient is consistent with a quasi-reversible charge transfer mechanism where the products and reactants do not vary significantly in structure.

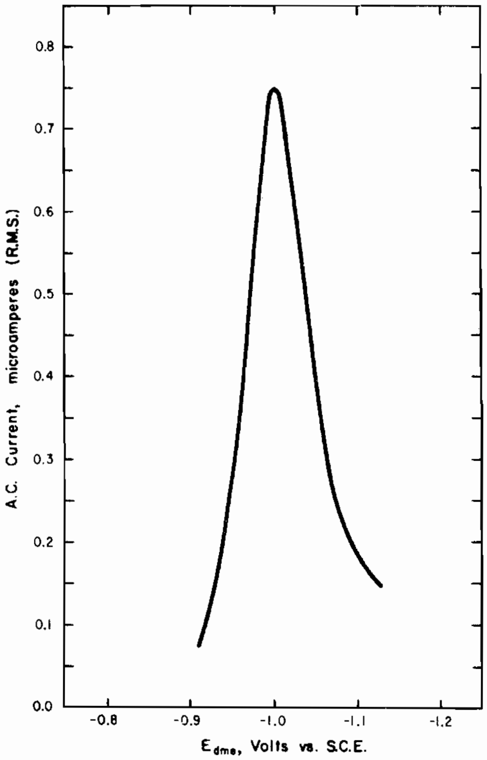

Figure 6. Phase selective AC polarogram for the faradaic process of $Co(terpy)_2^{2+}$. Applied potential: 20 Hz, 10 mv peak-to-peak a.c. signal, 50 mv min^{-1} d.c. scan rate. (The potential axis is referred to S.C.E. with saturated NaCl, —12 mv *vs.* S.C.E.).

Acknowledgment. We wish to express our gratitude to J. Judge and W. A. Baker, Jr. for providing the cobalt complex for our study and for stimulating our interest in these compounds.

---

[17] D. E. Smith in « Electroanalytical Chemistry », Vol. I, A. J. Bard, Ed., M. Dekker, Inc., New York, N. Y. (1966), p. 23.