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

Polarographic Behavior of the Bis(2,2′,2″-Terpyridine) Iron(II) Cation

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

Received December 27, 1968

The polarographic reduction of $Fe(terpy)_2^{2+}$ in aqueous solution was studied, using AC and DC techniques. One diffusion controlled wave was observed, preceded by a small adsorption wave. The principal wave was seen to be the result of a reversible two electron reduction. A zero-valent iron terpyridyl complex is postulated as the electrode reduction product. Values are obtained for the heterogeneous rate constant and the transfer coefficient for the principal wave.

Introduction

The tridentate ligand 2,2′,2″-terpyridine (terpy)[1] is known to form stable complexes with first row transition metal ions.[2] Similar complexes involving the ligands bipyridine and phenanthroline are also well known. The reductions and oxidations of these and related compounds have been studied by polarographic methods. Tanaka *et al.*[3] have examined the reduction of Fe $(bipy)_3^{2+}$ in acetonitrile solution and have detected low valence states of the complex. Similarly, the electrochemical oxidation of $Fe(bipy)_3^{2+}$ in aqueous medium has been reported by Pantini and Ciantelli.[4]

Recently, polarographic studies have been carried out in this laboratory,[5] concerning the behavior of the cobaltous complex, $Co(terpy)_2^{2+}$, in aqueous solution. Evidence was given for the existence of a Co^I - terpyridyl complex. The purpose of the present investigation is to report the polarographic behavior of the bis (2,2′,2″-terpyridine) iron(II) cation. Comparisons will be made to the $Co(terpy)_2^{2+}$ system.

Experimental Section

Chemicals. The $Fe(terpy)_2(ClO_4)_2$ was synthesized by W. Reiff and donated by W. A. Baker, Jr. The tetra-*n*-butyl ammonium chloride was Polarographic Grade and was used as received from the Southwestern Analytical Chemical Company, Austin, Texas. Conductivity water with a specific resistance of two megohms/cm was used to dissolve the complex. The measured pH of the $Fe(terpy)_2^{2+}$ solutions was 6.8.

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 from Philbrick Researches solid state operational amplifiers and standard electronic components. The AC polarograph was modified after instruments described by Hayes and Reilley[6] and Smith.[7] 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. 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

A DC polarogram of the iron complex in 0.1 *M* tetra-*n*-butyl ammonium chloride is shown in Figure 1. A small pre-wave is seen at about −1.3v *vs* SCE prior to the principal wave at −1.36v *vs* SCE. In Figure 2 can be seen a typical AC polarogram of $Fe(terpy)_2^{2+}$ showing the two waves with corresponding peak potentials of −1.3 and −1.36 *vs* SCE. Curve 1 is obtained at 20 Hz, and curve 2 at 500 Hz.

Both DC and AC measurements indicate that the pre-wave is the result of an adsorption process, and contributes a negligible fraction of faradaic current to the electron transfer process. This situation is analogous to the one shown by the cobalt complex, $Co(terpy)_2^{2+}$, previously reported.[5] Consequently, the main wave of the polarogram of $Fe(terpy)_2^{2+}$ will be the only one considered in the present discussion.

A plot of E *vs* $\log[i/(i_d-i)]$ from the DC polarogram of Figure 1 gives a straight line with a slope of 32 mv indicating a reversible, two electron reduction of the $Fe(terpy)_2^{2+}$ species. This is shown in Figure 3. A similar analysis can be made from the AC polarogram of Figure 2, where greater resolution of the main wave ($E_p = -1.36$v *vs* SCE) and the pre-wave

---

[1] G. Morgan and F. Burstall, *J. Chem. Soc.*, 1649 (1937).
[2] G. Morgan and F. Burstall, *J. Chem. Soc.*, 1672 (1938).
[3] N. Tanaka and Y. Sato, *Electrochimica Acta*, 13, 335 (1968).
[4] F. Pantini and G. Ciantelli, *J. Electroanal. Chem.*, 14, 423 (1967).
[5] D. J. Macero, F. V. Lovecchio, and S. J. Pace, *Inorg. Chim. Acta*, 3, 65, (1969).
[6] T. W. Hayes and C. N. Reilley, *Anal. Chem.*, 37, 1322 (1965).
[7] D. E. Smith, *Anal. Chem.*, 35, 1811 (1963).

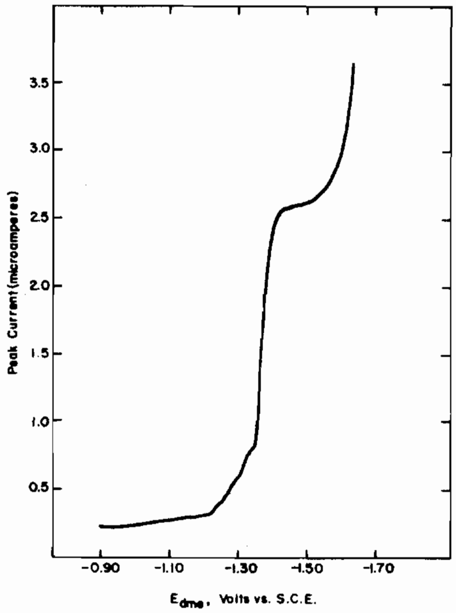

Figure 1. DC polarogram of 0.46 m*M* $Fe(terpy)_2^{2+}$ in 0.1 *M* tetra-*n*-butyl ammonium chloride.

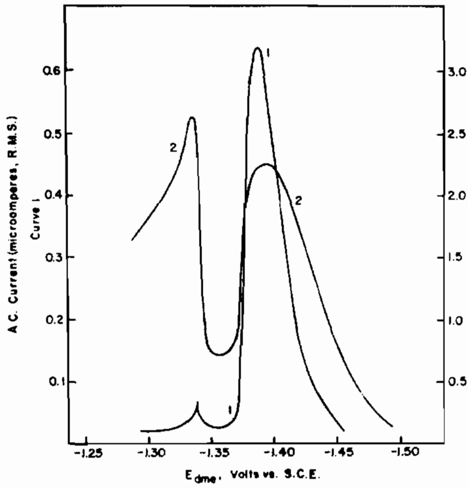

Figure 2. Fundamental harmonic phase-selective AC polarogram of 0.61 m*M* $Fe(terpy)_2^{2+}$ in 0.1 *M* tetra-*n*-butyl ammonium chloride. Applied potential: 5 mv peak-to-peak a.c. signal. Curve 1: 20 Hz. Curve 2: 500 Hz. 50 mv min^{-1} d.c. scan rate.

($E_p = -1.3$v *vs* SCE) can be achieved. A plot of the difference between the DC half-wave potential and the AC peak potential *vs* $\log\left[\left(\frac{I_p}{I}\right)^{1/2} - \left(\frac{I_p - I}{I}\right)^{1/2}\right]$ for a reversible process should yield two converging straight lines, the theoretical slope of each line being equal to (120/n) mv at low frequencies.[8] The point of convergence is the measured DC half-wave potential. The result of such a plot for $Fe(terpy)_2^{2+}$ is shown in Figure 4. The straight line slope is 62.5 mv, which is in good agreement with the expected value for a reversible two electron transfer process.

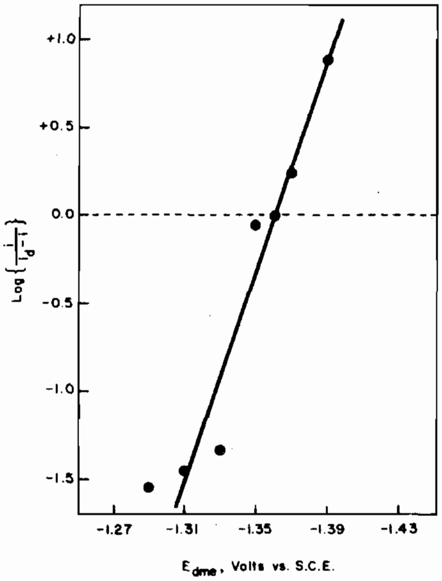

Figure 3. Plot of $\log\left(\frac{i}{i_d - i}\right)$ *vs.* potential for the DC polarogram of Figure 1.

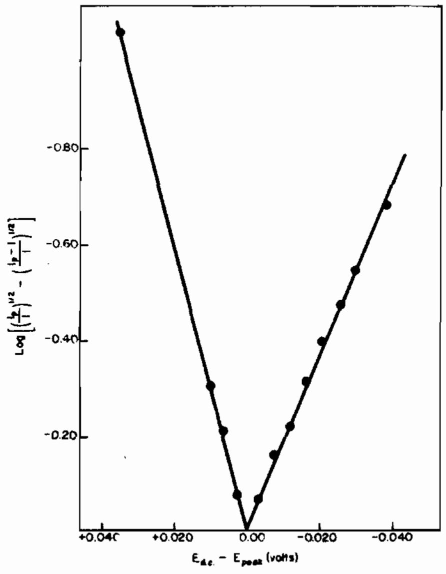

Figure 4. Plot of the difference between the DC half-wave potential and the AC peak potential versus $\log\left[\left(\frac{I_p}{I}\right)^{1/2} - \left(\frac{I_p - I}{I}\right)^{1/2}\right]$ from fundamental a.c. polarograms of $Fe(terpy)_2^{2+}$. Applied potential 20 Hz, 5 mv peak-to-peak a.c. signal. I = faradaic current component in phase with applied potential at end of natural drop-life.

Further analysis of the AC polarogram obtained at a frequency of 500 Hz gives a value of 0.5 for $k_{s,h}$, the heterogeneous rate constant, and a value of 0.47 for α, the transfer coefficient. These values imply that the reduction of $Fe(terpy)_2^{2+}$ proceeds rapidly and reversibly at the electrode surface at the frequencies employed, and that the assumption of Nernstian behavior for the DC polarographic process is valid.

---

(8) J. R. Delmastro and D. E. Smith, *Anal. Chem.*, 39, 1050 (1967).

The limiting current of the DC polarogram is directly proportional to the concentration of the iron complex, from 0.1 mM to 1.0 mM Fe(terpy)$_2^{2+}$. This is shown in Figure 5, along with similar results obtained for the bis(2,2′,2″-terpyridine) cobalt(II) cation. It can be seen from this graph that the slopes for the two curves are in the ratio 2 : 1. This is consistent with the postulations of two and one electron reduction mechanisms for the Fe(terpy)$_2^{2+}$ and Co(terpy)$_2^{2+}$ systems, respectively.

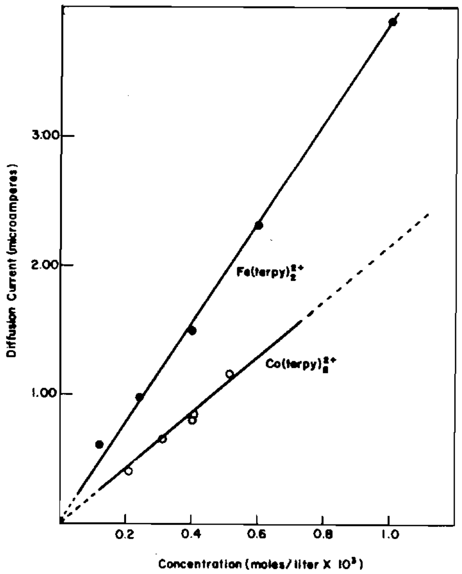

Figure 5. Plot of diffusion current versus concentration for Co(terpy)$_2^{2+}$ and Fe(terpy)$_2^{2+}$. Co(terpy)$_2^{2+}$ solutions in borate buffer background. Fe(terpy)$_2^{2+}$ solutions in tetra-*n*-butyl ammonium chloride background. 0.4 mM Co(terpy)$_2^{2+}$ solution run in borate buffer and also in tetra-*n*-butyl ammonium chloride background electrolyte.

Also, a polarogram was taken on a 1.0 mM solution of Fe(H$_2$O)$_6^{2+}$, which is known to produce zero valent iron as a reduction product.[9] Comparison with a polarogram of 1.0 mM Fe(terpy)$_2^{2+}$ showed diffusion currents of 4.8 μA and 3.9 μA for the aquo complex and the terpyridyl complex, respectively. If one assigns reasonable diffusion coefficients to these species, the observed diffusion currents are seen to be consistent with a two electron reduction mechanism in each case. A D value of 7.0×10^{-6} cm^2/sec was used for Fe(H$_2$O)$_6^{2+}$, while a value of 4.6×10^{-6} cm^2/sec was assigned to Fe(terpy)$_2^{2+}$, equating it to that given[4] to an ion of similar charge, size, and structure, *i.e.*, Fe(dipy)$_3^{2+}$.

Lastly, AC polarograms similar to Figure 2 show only a single, sharp peak for the faradaic process of Fe(terpy)$_2^{2+}$, at frequencies ranging from 20 Hz to 500 Hz. This indicates that only one electrode reduction occurs in the limiting current region of interest,[10] *i.e.*, that of Fe(terpy)$_2^{2+}$.

The free ligand exhibits polarographic activity in the same potential region as the complex. The DC polarogram of millimolar concentrations of the ligand alone produces an ill-defined multiple wave, the current heights of which are significantly higher than those obtained for the reduction of Fe(terpy)$_2^{2+}$. In fact, a polarogram of a solution containing 0.6 mM Fe(terpy)$_2^{2+}$ and 0.6 mM terpyridine shows that the well defined reduction wave of the complex is completely masked by the reduction of the ligand. Polarograms of solutions containing Fe(terpy)$_2^{2+}$ with no excess ligand showed no visible reduction of terpyridine.

Consideration of these facts leads to the postulation of an electrode reaction which excludes reduction of the ligand itself. In simplest form, this can be expressed by the following scheme:

$$\mathrm{Fe(terpy)_2^{2+}} + 2e^- = \mathrm{Fe(terpy)_2}$$

Other workers[3] have detected the existence of the tris(2,2′-bipyridine) iron(0) species by polarographic methods in acetonitrile solution. M. Falqui reports[11] a two electron reduction of Fe(bipy)$_3^{2+}$ in aqueous solution, but does not speculate on the nature of the product. An actual preparation of Fe(bipy)$_3$ in tetrahydrofuran has been reported[12] by Herzog and coworkers, and also in anhydrous dimethoxyethane[13] by Hall and Reynolds.

The delocalization of electron density by the π bonding network of the terpyridine ligand system may contribute to the relative stability of Fe(terpy)$_2$ in aqueous solution. That this effect is operative can be inferred from visible absorption spectra. Aqueous Fe(terpy)$_2^{2+}$ exhibts absorption peaks in the visible region,[14] with an ε_{max}, at 552 mμ, of $1.16 \times 10^4\ M^{-1}$ cm^{-1}. Similarly, solutions of Fe(bipy)$_3^{2+}$ display a visible spectrum[15] with an ε_{max}, at 522 mμ, of $0.85 \times 10^4\ M^{-1}$ cm^{-1}. These intense peaks have been interpreted[16] to be a result of charge transfer transitions of the type $t_{2g(\text{metal ion})} \rightarrow \pi^*_{(\text{ligand})}$. The shift of λ_{max} to longer wavelengths for Fe(terpy)$_2^{2+}$ is attributed to the greater electron acceptor character of the terpyridine ligands.

It is also interesting to note that the Mössbauer spectrum of the solid state complex, Fe(terpy)$_2$(ClO$_4$)$_2$, shows[17] an isomer shift (δ) of +0.29 mm/sec relative to natural iron foil, at 78°K. The same parameter for Fe(bipy)$_3$(ClO$_4$)$_2$ was measured[18] to be equal to +0.34 mm/sec. Since a more negative value of the isomer shift is an indication of greater s electron density at the iron nucleus, the observed differences in δ suggest[17,19] more extensive π delocalization of the « metal ion d electrons » in the iron terpyridyl complex.

---

(9) L. Meites, *Polarographic Techniques*, 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1965, p. 656.

(10) H. L. Hung and D. E. Smith, *J. Electroanal. Chem.*, *11*, 237, 425 (1966).

(11) M. T. Falqui, *Gazz. Chim. Ital.*, *88*, 57 (1958).

(12) S. Herzog and H. Präkel, 8th International Conference on Coordination Chemistry, Vienna, Sept. 7-11, 1964, p. 214.

(13) F. S. Hall and W. L. Reynolds, *Inorg. Chem.*, *5*, 931 (1966).

(14) R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 341 (1962).

(15) F. Wm. Cagle and G. F. Smith, *J. Amer. Chem. Soc.*, *69*, 1860 (1947).

(16) R. J. P. Williams, *J. Chem. Soc.*, 137 (1955).

(17) W. Reiff, Ph. D. Thesis, Syracuse University, Syracuse, N. Y., 1968.

(18) R. L. Collins, R. Pettit, and W. A. Baker, Jr., *J. Inorg. Nucl. Chem.*, *28*, 1001 (1966).

(19) W. A. Baker, Jr., Syracuse University, Private Communication, 1968.