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Polarographic and ESR Studies on the Electrode Reactions of Tris(2,2′-bipyridine)iron(II) in Acetonitrile

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In a previous paper[1] it was reported that in acetonitrile tris(2,2′-bipyridine)iron(II) was reduced to iron(I), iron(0) and iron(—I) complexes at the dropping mercury electrode. In that study, however, those complexes which were considered to be formed at the electrode were not isolated and their oxidation states were not confirmed by other techniques.

In this study the reduction products of tris(2,2′-bipyridine)iron(II) ($[Fe(bipy)_3]^{2+}$) were obtained by controlled potential electrolysis in acetonitrile and their ESR spectra were measured to clarify the oxidation states of those reduction products.

Experimental

Tris(2,2′-bipyridine)iron(II) perchlorate, $[Fe(bipy)_3](ClO_4)_2$, was synthesized according to the literature.[2] Acetonitrile was purified by the method presented by Coetzee.[3]

The polarographic measurement was carried out using an H-type cell and an aqueous saturated calomel electrode (SCE) at 25 °C. ESR spectra of reduction products which were obtained by controlled potential electrolysis were measured by the method of Geske and Maki[4] with an X-band JEOL P-10 ESR spectrometer and Mn^{2+} in MgO as standard.

Results and Discussion

A direct current (d.c.) polarogram of $[Fe(bipy)_3]^{2+}$ in acetonitrile with 0.05M $(C_2H_5)_4NClO_4$ as supporting electrolyte gave six reduction waves, although the sixth wave was not well-defined, as shown in Fig. 1 (Curve a). The limiting current of each of the first three waves was found to correspond to the value of one-electron reduction, while those of the fourth and fifth wave

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[4] D. H. Geske and A. H. Maki, *J. Amer. Chem. Soc.*, **82**, 2671 (1960).

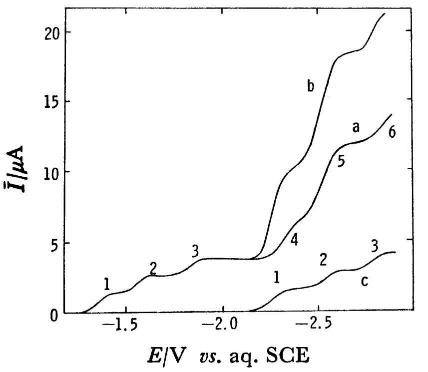

Fig. 1. D.c. polarograms of [Fe(bipy)$_3$](ClO$_4$)$_2$ and 2,2′-bipyridine in acetonitrile with 0.05 M (C$_2$H$_5$)$_4$NClO$_4$. (a) 0.5 mM [Fe(bipy)$_3$](ClO$_4$)$_2$, (b) a+0.6 mM 2,2′-bipyridine and (c) 0.3 mM 2,2′-bipyridine. Residual current and IR drop are corrected.

were those of two- and six-electron reduction, respectively. On the addition of free 2,2′-bipyridine the wave heights of the last three waves increased, as seen from Curve b in Fig. 1. The ligand itself undergoes reduction in acetonitrile at −2.24, −2.53, and −2.77 V *vs.* aq. SCE with the limiting current ratio of 1: 1: 1 (see Curve c in Fig. 1). Half-wave potentials of the reduction waves of [Fe(bipy)$_3$]$^{2+}$ and those of 2,2′-bipyridine in acetonitrile are given in Table 1. These experimental results suggested that the last three waves must be attributed to the reduction ofligand coordinated in and/or dissociated from the complex. Although the first three waves are considered to be due to the reduction of tris(2,2′-bipyridine)iron complex,[1] their electron transfer mechanisms are still in question; it has not been decided whether electrons enter to the ligand orbitals or to the metal ones.

Table 1. Half-wave potentials of reduction waves of [Fe(bipy)$_3$](ClO$_4$)$_2$ and 2,2′-bipyridine

Electrolytic solution[a]	Half-wave potential/V *vs.* aq. SCE				
	1st	2nd	3rd	4th	5th
I	−1.35	−1.55	−1.82	−2.32	−2.52
II				−2.26	−2.51
III	−2.24	−2.53	−2.77		

a) I: 0.5 mM [Fe(bipy)$_3$](ClO$_4$)$_2$+0.05 M (C$_2$H$_5$)$_4$NClO$_4$.
II: I+0.6 mM 2,2′-bipyridine.
III: 0.3 mM 2,2′-bipyridine+0.05 M (C$_2$H$_5$)$_4$NClO$_4$.

In order to obtain the definitive information of the nature of the reduction products, ESR spectra of the reduction products which were obtained by controlled potential electrolysis at various potentials were measured at room temperature.

The parent complex [Fe(bipy)$_3$]$^{2+}$, which has been reported to be diamagnetic[2], gave no ESR signal. A solution of reduction product obtained by electrolysis at −1.45 V, where a univalent complex [Fe(bipy)$_3$]$^+$ was considered to be formed, was purple and gave an ESR signal shown in Fig. 2. The g-value and the peak to peak width (ΔH_{msl}) were calculated to be 1.995_4 and 97 gauss, respectively. From the polarographic results and from the evidence that the intensity of this signal did not change by the addition of excess free 2,2′-bipyridine, the signal of $g=1.995_4$ was considered to be due to [Fe(bipy)$_3$]$^+$.

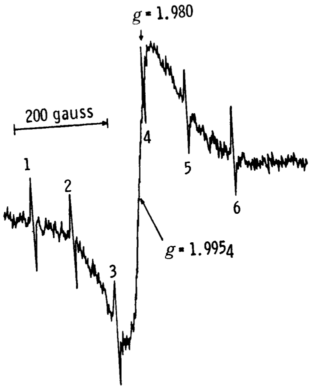

Fig. 2. ESR spectrum of the reduction product of [Fe(bipy)$_3$]-(ClO$_4$)$_2$ obtained by electrolysis at −1.45 V *vs.* aq. SCE. Signals of 1 to 6 are the hyperfine structures of Mn^{2+}.

It is known that most of the d^7 metal ions give g-values much greater than 2[5]. Goodman and Raynor[6], however, suggested that six-coordinated nominally d^7 spin-paired ion would give a low g-value if suitable π-bonded ligands were present with low-lying π^* orbitals available.

In the case of [Fe(bipy)$_3$]$^+$ which has a low g-value, therefore, it seems reasonable to consider that the iron exists as Fe^{2+} (d^6, spin-paired) and an unpaired electron is localized mainly on the ligand orbitals, because 2,2′-bipyridine possibly has low-lying vacant π^* orbitals.

On electrolysis at −1.70 V, where the formation of [Fe(bipy)$_3$] was expected, black crystals grew up at the surface of the mercury electrode and the solution which was in contact with the crystals was purple. In this case, two ESR signals were observed; one had a g-value of 1.995_4 and the other, a g-value of 2.08 and ΔH_{msl} of about 800 gauss. The former signal was the same as that of [Fe(bipy)$_3$]$^+$, while the latter was found to coincide with that of [Fe(bipy)$_3$] reported by Hall and Reynolds[7]. These results seem to support that [Fe(bipy)$_3$] was formed at the potential of the second wave and that [Fe(bipy)$_3$] reacts with [Fe(bipy)$_3$]$^{2+}$ to form [Fe(bipy)$_3$]$^+$ in solution. The ESR signal of g-value of 2.08 suggested that [Fe(bipy)$_3$] has the iron of d^8 configuration, although the optical spectrum of [Fe(bipy)$_3$] obtained in 1,2-dimethoxyethane indicated that the unpaired electrons exist also in the ligand orbital.[7,8]

The brown solution of reduction product generated by electrolysis at −2.10 V gave ESR spectrum with g-value of 1.995_4 and ΔH_{msl} of 14 gauss both in the absence and in the presence of free 2,2′-bipyridine as shown in Fig. 3.

The g-value found for this product did not coincide with the reported value of 2.0031 for the solid of Na-[Fe(bipy)$_3$],[8] in spite of the expectation of the formation of [Fe(bipy)$_3$]$^-$ complex at this potential. The dif-

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6) B. A. Goodman and J. B. Raynor, *J. Chem. Soc., Ser. A*, **1970**, 2038.

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

8) C. Mahon and W. L. Reynolds, *ibid.*, **6**, 1927 (1967).

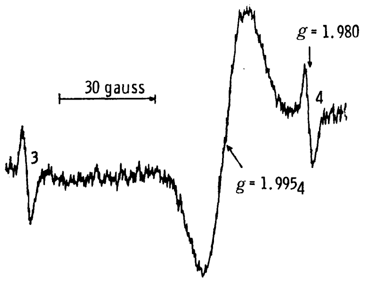

Fig. 3. ESR spectrum of the reduction product of $[Fe(bipy)_3]$-$(ClO_4)_2$ obtained by electrolysis at −2.10 V *vs.* aq. SCE. Signals of 3 and 4 are the hyperfine structures of Mn^{2+}.

ference between the observed *g*-value and the reported one is now under consideration.

The fact that, at the beginning of electrolysis at −2.10 V, ESR spectra with *g*-values of 1.995_4 and 2.08, which corresponded to those of $[Fe(bipy)_3]^+$ and $[Fe(bipy)_3]$ respectively, were also obtained seems to support proportionation reactions between the products and the parent complex taking place.

At −2.40 V, the formation of two kinds of reduction products was observed. One was the same as the product obtained by electrolysis at −2.10 V and the other was considered to be bipyridine anion radical from its *g*-value. Only the latter signal increased its intensity by continued electrolysis. This supports that bipyridine and/or its anion radical were formed by the dissociation of the reduction product such as $[Fe(bipy)_3]^{2-}$ either at the electrode surface or in the solution. Bipyridine anion radical was obtained in acetonitrile by electrolysis of 2,2′-bipyridine at −2.40 V and gave ESR spectrum with *g*-value of 2.003_6 and ΔH_{msl} of 7.5 gauss.

In conclusion, it should be emphasized that the observations mentioned above are in a sharp contrast with those in aqueous solutions, because in aqueous solutions the complexes of low oxidation states such as $[Fe(bipy)_3]^+$ and $[Fe(bipy)_3]^-$ are considered not to be formed electrochemically either at the electrode surface or in the solution.

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