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The Electrochemical Behavior of the Low-valent Transition Metal Complexes. II. Iron(0)-2,2′-Bipyridine Complexes

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The electroreduction reaction of the zero-valent iron-2,2′-bipyridine complexes ($Fe(bipy)_2$ and $Fe(bipy)_3$) was studied in a hexamethylphosphoric triamide solution by polarography and ESR measurements. In the polarography, $Fe(bipy)_2$ was first reduced at a very less negative potential ($E_{1/2} = -0.76$ V *vs.* Hg pool) than the first wave potential of free bipyridine (-2.37 V *vs.* Hg pool). In the presence of excess bipyridine, $Fe(bipy)_2$ was first reduced at -1.10 V *vs.* Hg pool corresponding to the second reduction step of the solution of $Fe(bipy)_2$. The visible spectra of the solution of $Fe(bipy)_2$ in the presence of excess bipyridine was different from that of the solution of $Fe(bipy)_2$ only. The signal with hyperfine structure attributable to the anion radical of bipyridine was observed by means of ESR analysis of the solution electrolyzed at the potential corresponding to the second reduction step. From these results, it was concluded that $[Fe(bipy)(HMPT)_m]$ was reduced at the first step, and $[Fe(bipy)_2(HMPT)]$ was reduced at the second.

Although many electrochemical studies on high-valent transition metal complexes have been reported,[1,2] only a few studies on the electrochemical behavior of low-valent transition metal complexes have been carried out. It seemed that it would be interesting to perform a study of the electrochemical behavior of low-valent transition metal complexes in relation to evaluation of the charge distribution and the stability of the reduced complexes.

In a previous paper,[3] we reported a study on the electrochemical behavior of the low-valent nickel-2,2′-bipyridine complexes. In this paper, the electrochemical study on the zero-valent iron-2,2′-bipyridine complexes will be described.

Experimental

Materials. Hexamethylphosphoric triamide (HMPT) used as solvent was refluxed over calcium hydride for several hours and was then fractionally distilled under a reduced nitrogen pressure. Tetra-*n*-butylammonium perchlorate (TBAP) was prepared by the published method.[3] 2,2′-Bipyridine was used as purchased, mp 69.5—70.0 °C.

The examined complexes were bis(2,2′-bipyridine)iron(0) ($Fe(bipy)_2$), and tris(2,2′-bipyridine)iron(0) ($Fe(bipy)_3$). $Fe(bipy)_2$ was obtained by heating a benzene solution of diethylbis(2,2′-bipyridine)iron(II) ($Et_2Fe(bipy)_2$) at 50 °C for several hours.[4] $Fe(bipy)_3$ was obtained by decomposing $Et_2Fe(bipy)_2$ in the presence of excess bipyridine at 50 °C for several hours.[4] Tris(2,2′-bipyridine)iron(II) perchlorate ($[Fe(bipy)_3](ClO_4)_2$) was prepared according to the method of Nyholm *et al.*[5]

Apparatus and Procedure. The polarographic analysis was performed using an H-type cell. The cathode and the anode were a dropping mercury and a mercury pool, respectively. The concentration of the complexes was generally 5.0×10^{-3} mol/l, while that of TBAP was 2.0×10^{-1} mol/l. The polarograph used was a Yanagimoto Model PB-105. For the ESR analysis, an electrolytic cell as shown in the previous paper[3] was used. The ESR spectra were recorded on a JEOL Model JS-3BS-X Spectrometer. The visible spectra of the complex solution were measured using a Shimadzu Model MPS-50L Spectrophotometer. All operations were handled under nitrogen purified by activated copper.

Results and Discussion

Polarographic Results on the Complexes. The complex $Fe(bipy)_2$ is stable in non-polar solvents such as benzene and tetrahydrofuran, but it is unstable in polar solvents such as 1,2-dimethoxyethane, acetonitrile, and HMPT. The color of the HMPT solution of $Fe(bipy)_2$ changed from brown to violet, and lastly a yellow precipitate was produced under nitrogen at room temperature within a few hours. Therefore the polarographic measurement of the complexes was performed quickly. The polarographic results on the complexes are shown in Table 1.

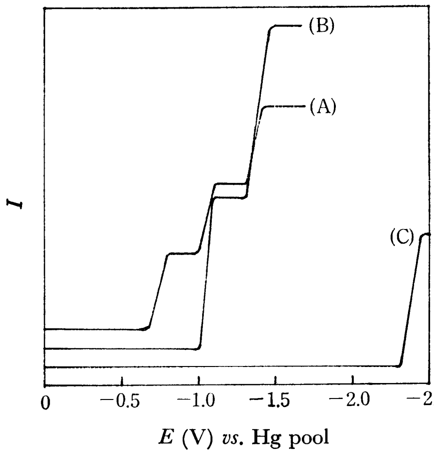

Fig. 1. Polarogram of $Fe(bipy)_2$ in the presence of bipyridine. (A): $Fe(bipy)_2$, (B): Addition of 10-fold molar amount of bipyridine, (C): Free bipyridine.

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[1] N. Tanaka, and Y. Sato, *Inorg. Nucl. Chem. Lett.*, **2**, 359 (1966); *ibid.*, **4**, 487 (1968); Y. Sato, and N. Tanaka, This Bulletin, **42**, 1021 (1969); *ibid.*, **41**, 2059, 2064 (1968).

[2] N. Tanaka, and Y. Sato, *Electrochim. Acta*, **13**, 335 (1968).

[3] A. Misono, Y. Uchida, Y. Yamagishi, and H. Kageyama, This Bulletin, **45**, 1438 (1972).

[4] A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, and A. Misono, *J. Amer. Chem. Soc.*, **90**, 1878 (1968).

[5] F. H. Burstall, and R. S. Nyholm, *J. Chem. Soc.*, **1952**, 3570.

Table 1. Polarographic results on the complexes

Complex	$E_{1/2}(1)$[b]	$E_{1/2}(2)$[b]	$E_{1/2}(3)$[b]	Wave height ratio
Fe(bipy)$_2$	-0.76	-1.08	-1.40	1.0 : 0.9 : 1.0
Fe(bipy)$_2$ + bipy[a]	-1.10	-1.41		1.0 : 0.9
Fe(bipy)$_3$	-1.89			
[Fe(bipy)$_3$](ClO$_4$)$_2$	-1.29	-1.53	-1.85	1.0 : 1.0 : 1.0
	(-1.34)[c]	(-1.55)[c]	(-1.89)[c]	
Free bipyridine	-2.37	-2.80		1.0 : 0.7

Conditions: cathode, a dropping mercury electrode; anode, a mercury electrode; solvent, hexamethylphosphoric triamide; concentration of the complex, 5.0×10^{-3} mol/l; supporting electrolyte, $(n\text{-}C_4H_9)_4N^+ClO_4^-$ (TBAP); concentration of TBAP, 2.0×10^{-1} mol/l.

a) Fe(bipy)$_2$: bipy=1.0: 10 (molar ratio) b) Potential *versus* Hg pool c) Ref. 2.

The first half-wave potential ($E_{1/2}(1)$) of Fe(bipy)$_2$ appeared at a far less negative potential (−0.76 V *vs.* Hg pool) than $E_1/_2(1)$ of free bipyridine. The reduction step of the complex was less reversible, but the electron to be transferred was supposed to be one from the slope of the reduction wave. The ratio of the heights of the first and the second waves was 1.0: 0.9, and the slope of the second wave indicates a one-electron transfer in the second as well as in the first.

When a 10-fold molar amount of bipyridine was added to the complex solution, the decomposition of the complex was suppressed, and the first wave appeared at −1.10 V *vs.* Hg pool corresponding to the second reduction step of the solution of Fe(bipy)$_2$ as shown in Fig. 1. The second wave appeared at −1.41 V *vs.* Hg pool corresponding to the third reduction step of the solution of Fe(bipy)$_2$. The addition of bipyridine increased the height of the second and the third waves of the solution of Fe(bipy)$_2$ only. Furthermore these waves became reversible as their height was increased by the addition of bipyridine as shown in Table 2. The change in the height and reversibility of the second and the third waves suggests that added bipyridine takes part in these reduction steps.

Table 2. Effect of addition of bipyridine on the second reduction wave of Fe(bipy)$_2$ in HMPT

Molar ratio		Relative wave height[a]	Slope (mV)[b]
bipy/Fe(bipy)$_2$	0	—	91.2
bipy/Fe(bipy)$_2$	10	2.2	73.4
bipy/Fe(bipy)$_2$	100	4.0	65.0

Conditions: cathode, a dropping mercury; anode, a mercury pool; concentration of the complex, 5.0×10^{-3} mol/l; concentration of TBAP, 2.0×10^{-1} mol/l.

a) The ratio of the height of the first wave in the presence of excess bipyridine to the height of the second wave in the absence of bipyridine b) Value in the log-plot analysis

The reduction waves of the solution of Fe(bipy)$_2$ at a considerably negative potential could not be successfully observed because of the disturbance in the wave shapes. The reduction wave of free bipyridine was observed after the wave in which the complex was considered to take part. After a prolonged reduction of the complex solution at about −2.0 V *vs.* Hg pool, the color of the solution faded and the resulting polarogram showed only the reduction waves of free bipyridine. These results may be attributable to the instability of the reduced species in spite of the presence of a large amount of bipyridine.

The Visible Spectra of the Complex Solutions. The complex Fe(bipy)$_2$ is very slightly soluble in benzene, to give a blue-violet colored solution. This intense color is considered to be due to the charge transfer between the central metal atom and the ligand molecule.[6] However Fe(bipy)$_2$ was readily soluble in HMPT, to give a brown colored solution, and then decomposed into a yellow precipitate within a few hours under nitrogen at room temperature.

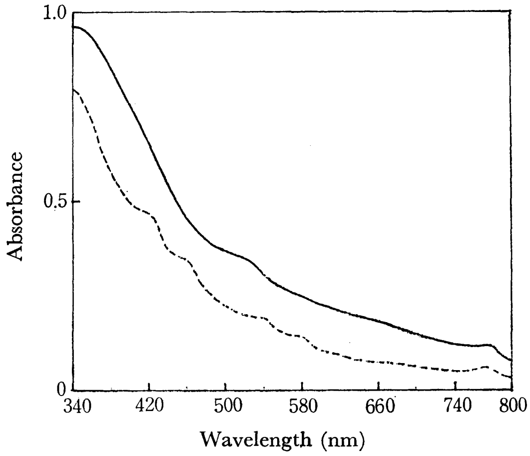

Fig. 2. The visible spectra of Fe(bipy)$_2$–HMPT solution.
——: Fe(bipy)$_2$ in HMPT
------: Fe(bipy)$_2$+10-fold molar amount of bipyridine in HMPT.

When excess bipyridine was added to the complex solution, the visible spectrum of the solution is different from that of the solution of Fe(bipy)$_2$ in the absence of bipyridine. These spectra are shown in Fig. 2.

When Et$_2$Fe(bipy)$_2$, Fe(bipy)$_2$, and Fe(bipy)$_3$ were used as the catalysts for the oligomerization of butadiene(BD), the reaction intermediate is considered to be [Fe(bipy)(BD)$_2$].[4] HMPT with a donor- and an acceptor-level can also coordinate to a low-valent transition metals. It is therefore reasonable to consider that the coordinated bipyridine is replaced by HMPT, and [Fe(bipy)(HMPT)$_m$] (m=1, 2, or 3) is produced in an HMPT solution.

Fe(bipy)$_3$ is very slightly soluble and stable in ben-

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[6] Y. Kaizu, T. Yazaki, Y. Torii, and H. Kobayashi, This Bulletin, **43**, 2068 (1970).

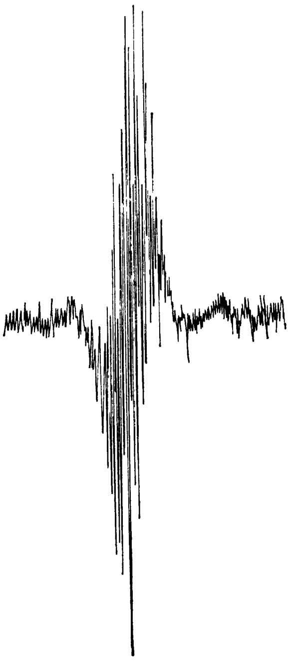


Fig. 3. ESR signal in the electrolysis of Fe(bipy)$_2$ at −1.30 V *vs.* Ag wire (*g*-value, 2.002$_5$).

zene and HMPT, to give a dark brown colored solution. The visible spectrum of the solution of Fe(bipy)$_3$ did not change by the addition of bipyridine.

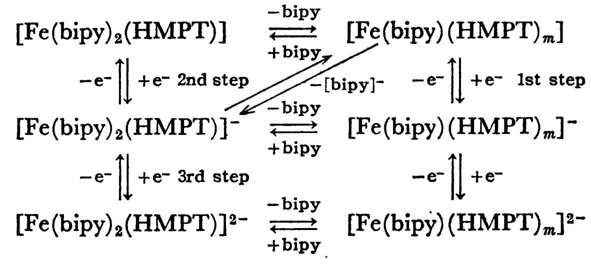
ESR Measurements. In the electrolysis of Fe(bipy)$_2$ in HMPT at the potential sufficiently negative to cause the first reduction step, no ESR signal was observed. However in the electrolysis at the potential corresponding to the second reduction step, the ESR signal with hyperfine structure attributable to the anion radical of 2,2′-bipyridine[7] was observed. This signal was stable in HMPT and was observed to be overlapped with another signal with an ill-defined structure. The observed signal is shown in Fig. 3. The similar signal was observed in the electrolysis of the nickel(0)-2,2′-bipyridine complexes in HMPT at the potential corresponding to the second reduction step.[3]

Taking into account the polarographic results at the second reduction step, it was concluded that the anion radical of bipyridine was formed by the dissociation of the species produced at the second reduction step.

Reaction Mechanism in the Electrolysis of Fe(bipy)$_2$. Taking into account the polarographic results and the visible spectra of the solution of Fe(bipy)$_2$, the following equilibrium in HMPT is proposed.

$$[\mathrm{Fe(bipy)_2(HMPT)}] \overset{\mathrm{HMPT}}{\rightleftarrows} [\mathrm{Fe(bipy)(HMPT)}_m] + \mathrm{bipy}$$

As a mechnism of the electro-reduction of Fe(bipy)$_2$ in HMPT, the following mechanism is proposed.



$$\begin{tikzcd}
{[\mathrm{Fe(bipy)_2(HMPT)}]} \arrow[r, shift left, "-\mathrm{bipy}"] \arrow[d, shift left, "+e^-\ \text{2nd step}"] & {[\mathrm{Fe(bipy)(HMPT)}_m]} \arrow[l, shift left, "+\mathrm{bipy}"] \arrow[d, shift left, "+e^-\ \text{1st step}"] \arrow[dl, "-[\mathrm{bipy}]^-"] \\
{[\mathrm{Fe(bipy)_2(HMPT)}]^-} \arrow[u, shift left, "-e^-"] \arrow[r, shift left, "-\mathrm{bipy}"] \arrow[d, shift left, "+e^-\ \text{3rd step}"] & {[\mathrm{Fe(bipy)(HMPT)}_m]^-} \arrow[u, shift left, "-e^-"] \arrow[l, shift left, "+\mathrm{bipy}"] \arrow[d, shift left, "+e^-"] \\
{[\mathrm{Fe(bipy)_2(HMPT)}]^{2-}} \arrow[u, shift left, "-e^-"] \arrow[r, shift left, "-\mathrm{bipy}"] & {[\mathrm{Fe(bipy)(HMPT)}_m]^{2-}} \arrow[u, shift left, "-e^-"] \arrow[l, shift left, "+\mathrm{bipy}"]
\end{tikzcd}$$

The complex Fe(bipy)$_2$ is unstable and gave a disturbed polarogram, from which no clear-cut information was obtained, but it showed more reduction waves at a potential more negative than the third reduction step, so a reduction state more than the third reduction state may be expected. Tris(2,2′-bipyridine)chromium(0) has previously been reported to be reduced to the hexa-anion stage, $\mathrm{Ca_3[Cr(bipy)_3]\cdot 7NH_3}$.[8]

The Electroreduction Reaction of Fe(bipy)$_3$ in HMPT. Tanaka *et al.*[2,9] reported that in the electroreduction of $\mathrm{[Fe(bipy)_3](ClO_4)_2}$ in acetonitrile, the following mechanism has been proposed.

$$[\mathrm{Fe(bipy)_3}]^{2+} + e^- \rightleftarrows [\mathrm{Fe(bipy)_3}]^{+}$$
$$E_{1/2} = -1.34\ \mathrm{V}\ \textit{vs.}\ \mathrm{SCE}$$
$$[\mathrm{Fe(bipy)_3}]^{+} + e^- \rightleftarrows [\mathrm{Fe(bipy)_3}]^{0}$$
$$E_{1/2} = -1.55\ \mathrm{V}\ \textit{vs.}\ \mathrm{SCE}$$
$$[\mathrm{Fe(bipy)_3}]^{0} + e^- \rightleftarrows [\mathrm{Fe(bipy)_3}]^{-}$$
$$E_{1/2} = -1.89\ \mathrm{V}\ \textit{vs.}\ \mathrm{SCE}$$

The first wave potential of Fe(bipy)$_3$ in HMPT appeared at −1.89 V *vs.* Hg pool. The visible spectrum of the solution of Fe(bipy)$_3$ is similar to that in benzene, and it did not change by the addition of free bipyridine. From the above results, the analogous reaction mechanism was proposed in the electrolysis of Fe(bipy)$_3$ in HMPT.

$$\mathrm{Fe(bipy)_3} + e^- \rightleftarrows [\mathrm{Fe(bipy)_3}]^-$$

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[7] N. Maki, T. Hirano, and S. Musha, *ibid.*, **36**, 756 (1963).

[8] S. Herzog, U. Grimm, and W. Waichenbauer, *Z. Chem.*, **7**, 355 (1967).

[9] N. Tanaka, T. Ogata, and N. Niizuma, The 18th Symposium on Polarography and Electric Analysis, Preprint p. 11, Tokyo (1972).