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Polarographic Behavior of Tris(2,2′-bipyridine)manganese(II) in Acetonitrile Solutions

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Polarographic behavior of tris(2,2′-bipyridine)manganese(II) perchlorate at the dropping mercury electrode in acetonitrile solutions has been investigated by the measurement of d.c., a.c. and Kalousek polarograms. The manganese(II) complex gave a five-step reduction wave and a one-step oxidation wave at the dropping mercury electrode when tetraethylammonium perchlorate was used as supporting electrolyte. In the presence of a large concentration of free 2,2′-bipyridine, the limiting currents of the first three steps of the reduction of the manganese(II) complex are all diffusion-controlled and of a one-electron reduction process. The electrode processes for these steps have been concluded to be the reductions to $[Mn(bipy)_3]^+$, $[Mn(bipy)_3]$ and $[Mn(bipy)_3]^-$, respectively.

The electro-reduction of tris(2,2′-bipyridine)manganese(II) complex at the dropping mercury electrode (DME) in ethanol solutions and the formation of tris(2,2′-bipyridine)manganese(I) cation, $[Mn(bipy)_3]^+$, at the electrode surface were briefly reported.[1]

In acetonitrile solutions the electro-reduction of tris(2,2′-bipyridine)manganese(II) complex is expected to proceed to the lower oxidation state as was observed with tris(2,2′-bipyridine)iron(II)[2] and tris(2,2′-bipyridine)cobalt(II)[3] complexes.

The present paper is concerned with the polarographic behavior of tris(2,2′-bipyridine)manganese(II) complex and the support on the formation of $[Mn(bipy)_3]$ and $[Mn(bipy)_3]^-$ at the DME in acetonitrile solutions.

Experimental

Tris(2,2′-bipyridine)manganese(II) perchlorate, $[Mn(bipy)_3](ClO_4)_2$ was prepared according to Burstall and Nyholm[4] and identified by chemical analysis. Acetonitrile, tetraethylammonium perchlorate and sodium perchlorate were the same as described in a previous paper.[2] The dropping mercury electrode used had an m value of 0.63_1 mg/sec and a drop time t_d of 4.83 sec when measured in an air-free acetonitrile solution

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[1] A. A. Vlček, *Pure and Applied Chem.*, **10**, 61 (1965).

[2] N. Tanaka and Y. Sato, *Inorg. Nucl. Chem. Letters*, **2**, 359 (1966); *Electrochim. Acta*, **13**, 335 (1968).

[3] N. Tanaka and Y. Sato, This Bulletin, **41**, 2059 (1968).

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

containing 0.05 M of $(C_2H_5)_4NClO_4$ at 25°C and at −0.5 V *vs.* SCE at 50 cm of the height of mercury reservior. An aqueous saturated calomel electrode (SCE) served as reference electrode. The electrolysis cell and other apparatus are previously reported.[2]

Results

Tris(2,2′-bipyridine)manganese(II) complex gave a five-step reduction wave with a maximum at the second step when tetraethylammonium perchlorate was used as supporting electrolyte (Fig. 1). In the solutions containing sodium perchlorate as supporting electrolyte only the first two steps were observed which were followed by the reduction of sodium ions.

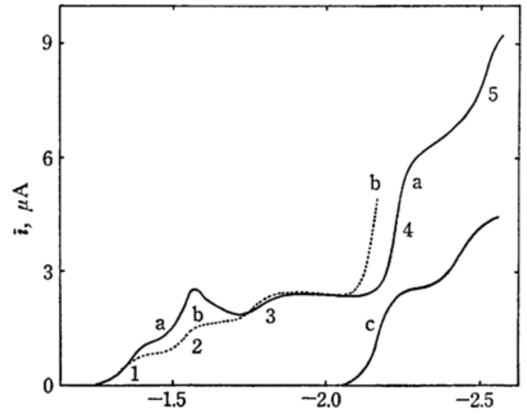

Fig. 1. D.c. polarograms of 0.5 mM $[Mn(bipy)_3](ClO_4)_2$ (a) in the absence and (b) the presence of 5.0 mM 2,2′-bipyridine and (c) that of 0.5 mM free 2,2′-bipyridine. Supporting electrolyte is 0.05 M $(C_2H_5)_4NClO_4$.

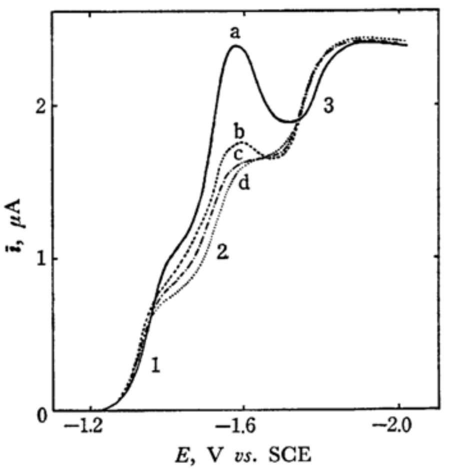

Fig. 2. The effect of free 2,2′-bipyridine upon the first three steps of the reduction wave of 0.5 mM $[Mn(bipy)_3](ClO_4)_2$. The concentrations of 2,2′-bipyridine are (a) 0, (b) 0.5 mM, (c) 1.0 mM and (d) 5.0 mM.

Table 1. Half-wave potentials and slopes of log-plots for the first step of the reduction wave of 0.5 mM $[Mn(bipy)_3](ClO_4)_2$ in acetonitrile solutions containing various concentrations of 2,2′-bipyridine and 0.05 M $(C_2H_5)_4NClO_4$ at 25°C.

Concn. of 2,2′-bipyridine mM	$E_{1/2}$ V *vs.* SCE	Slope mV
0	−1.347	69
0.5	−1.340	75
1.0	−1.335	71
2.0	−1.329	65
5.0	−1.333	65
10.0	−1.327	64

Upon the addition of free 2,2′-bipyridine, the maximum at the second step was depressed (Fig. 2) and the limiting currents of the fourth and the fifth step increased. In the presence of 5.0 mM or more, the reduction potentials and the limiting currents of the first three steps which are shown by curve **d** in Fig. 2 were almost the same irrespective of the concentration of bipyridine. Therefore, the nature of the limiting currents of the first three steps was investigated with the solutions containing excess 2,2′-bipyridine. The limiting currents of the first three steps were found to be proportional to the square root of the mercury pressure between 45 cm and 60 cm on the DME and also to the concentration of the complex. The results of log-plot analysis of the first step of the reduction at various concentrations of 2,2′-bipyridine are given in Table 1. At a large concentration of 2,2′-bipyridine compared with the complex, the half-wave potentials and the slopes of log-plot seem to be constant irrespective of the concentration of bipyridine. Free 2,2′-bipyridine gave a two-step reduction wave at the potentials where tris(2,2′-bipyridine)manganese(II) complex gave the fourth and the fifth wave, respectively, as shown in Fig. 1.

Upon the addition of a small concentration of water into the acetonitrile solution, the first three steps of the reduction wave were scarcely affected, but the fourth and the fifth step shifted to less negative potentials and the limiting currents increased as seen in the five-step reduction wave of tris(2,2′-bipyridine)iron(II) cmplex.[2]

The reversibilities of the first three steps were confirmed by the measurement of Kalousek polarograms, which are shown in Fig. 3. A one-step, a two-step and a three-step oxidation wave were obtained, when the electrode potentials were set up at −1.40 V, −1.65 V and −1.95 V respectively.

A.c. polarograms of the complex gave five peaks; their peak potentials were found to coincide with the half-wave potentials of the corresponding steps of the

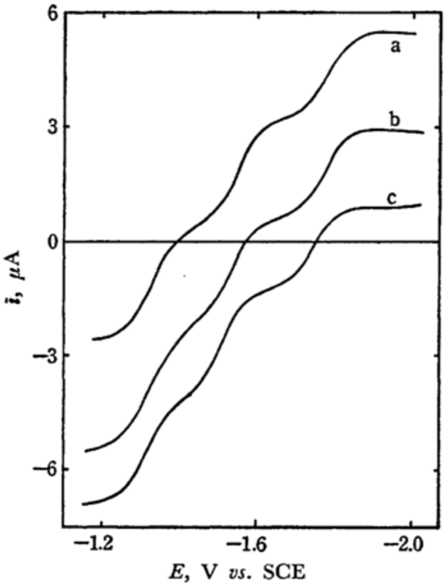

Fig. 3. Kalousek polarograms of the solution containing 0.5 mM $[Mn(bipy)_3](ClO_4)_2$, 50.0 mM 2,2′-bipyridine and 0.05 M $(C_2H_5)_4NClO_4$. Electrode potentials are set up at (a) −1.40 V, (b) −1.65 V and (c) −1.95 V. Exchange frequency is about 14 Hz.

d.c. polarogram. The addition of free 2,2′-bipyridine to the solution of the complex increased the fourth and the fifth peak current, but gave almost no influence on the first, the second and the third one.

The complex gave a one-step anodic wave at about +0.3 V which was almost the same as the potential of anodic wave of free 2,2′-bipyridine. However, neither the manganese(II) complex nor free 2,2′-bipyridine gave an anodic wave at less positive potentials than +1.9 V,[2] when the rotated platinum electrode was used as a working electrode.

Discussion

The limiting currents of the first three steps of the reduction wave of tris(2,2′-bipyridine)manganese(II) complex in the presence of excess 2,2′-bipyridine are concluded to be diffusion-controlled from the linearities of the limiting currents on the square root of the mercury pressure and the complex concentrations. The diffusion current constant for the first step calculated by the Ilkovič equation is 1.95, which is nearly equal to the values of one-electron reduction of various metal ions[5] and tris(2,2′-bipyridine)iron(II)[2] and tris(2,2′-bipyridine)cobalt(II)[3] in acetonitrile solutions. The ratio of the wave height for the first three steps obtained at a large concentration of 2,2′-bipyridine is 1 : 1 : 1 after corrected for the drop time. The slope of log-plot analysis for the first step approaches to the value of a reversible one-electron reduction with increasing concentrations of 2,2′-bipyridine (Table 1). 2,2′-Bipyridine seems to act as a maximum suppressor. The effect of 2,2′-bipyridine and water on the d.c. ploarogram suggests that the first three steps and other two steps observed at more negative potentials are different in nature from the same consideration as in the case with the reduction of the iron(II)[2] and the cobalt(II)[3] complexes. From all these results mentioned above, each of the first three steps of the manganese(II) complex is concluded to be a one-electron reduction of the complex itself as given by

$$[Mn(bipy)_3]^{2+} \underset{-e}{\overset{e}{\rightleftharpoons}} [Mn(bipy)_3]^{+} \underset{-e}{\overset{e}{\rightleftharpoons}}$$

$$[Mn(bipy)_3] \underset{-e}{\overset{e}{\rightleftharpoons}} [Mn(bipy)_3]^{-}$$

and the other two steps, the reduction of the ligand liberated from the complex. Kalousek polarograms show that the electrode process of each of the first three steps is reversible and also confirm the existence of low oxidation states such as $[Mn(bipy)_3]^+$, $[Mn(bipy)_3]$ and $[Mn(bipy)_3]^-$ at the electrode surface in acetonitrile.

The formation of tris(2,2′-bipyridine)manganese(I) state at the DME in ethanol was already reported by Vlcek,[1] though the compound seems not to be isolated. Herzog and Schmidt prepared tris(2,2′-bipyridine)manganese(0), $[Mn(bipy)_3]$,[6] and lithium tris(2,2′-bipyridine)manganate(−I), $Li[Mn(bipy)_3]$-4THF,[7] in tetrahydrofuran(THF). These facts confirm the above explanation for the first three steps of the reduction wave of the manganese(II) complex in acetonitrile. It may be concluded from the results obtained with the rotated platinum electrode that the anodic wave observed at +0.3 V is not the oxidation of manganese(II) to higher oxidation state but the oxidation of mercury to form mercury-bipyridine complexes, bipyridine being liberated from the manganese(II) complex at the electrode surface.

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6) S. Herzog and M. Schmidt, *Z. Chem.*, **2**, 24 (1962).

7) S. Herzog and M. Schmidt, *ibid.*, **3**, 392 (1963).