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Polarographic Behavior of Tris(2,2′-bipyridine)chromium(III) and Tris(ethylenediamine)chromium(III) in Acetonitrile Solutions

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Polarographic behavior of tris(2,2′-bipyridine)chromium(III) perchlorate and tris(ethylenediamine)chromium(III) perchlorate in acetonitrile solutions has been investigated by the measurement of d.c., a.c. and Kalousek polarograms. The bipyridine complex gives a six-step reduction wave when tetraethylammonium perchlorate is used as supporting electrolyte. The limiting currents of the first four steps are all diffusion-controlled, and each of them is of a one-electron reduction process. It has been proposed that at the fourth step univalent tris(2,2′-bipyridine)-chromate anions, $[Cr(bipy)_3]^-$, are formed at the electrode surface in acetonitrile. The limiting current of the one-electron reduction wave of tris(ethylenediamine)chromium(III) is increased upon the addition of 2,2′-bipyridine. It was explained as a reduction of an electroactive species, Cr(II)-bipyridine complex, which was formed by the reaction between Cr(II) produced by the reduction of tris(ethylenediamine)chromium(III) complex and 2,2′-bipyridine at the electrode surface.

As acetonitrile is an aprotic solvent and has less oxidizing power than water, the electrode process in acetonitrile is sometimes quite different in water. Tris(2,2′-bipyridine) complexes of manganese(II),[1] iron(II),[2] cobalt(II)[3] and nickel(II)[4] are reduced to the univalent anions at the dropping mercury electrode(DME). Such a low valent state is expected also in bipyridine complex of chromium.

In the present paper, the electrode processes of tris(2,2′-bipyridine)chromium(III) and tris-(ethylenediamine)chromium(III) are studied and the effect of 2,2′-bipyridine on the reduction wave of the latter complex is discussed. The support on the formation of tris(2,2′-bipyridine)chromate anion, $[Cr(bipy)_3]^-$, at the DME in acetonitrile solutions and an example of electrode process followed by chemical reaction involving electroactive species are presented.

Experimental

Tris(2,2′-bipyridine)chromium(III) perchlorate[5] and tris(ethylenediamine)chromium(III) perchlorate[6] were prepared and identified by elementary analysis. Other reagents 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 solutions containing 0.05 M of tetraethylammonium perchlorate, $(C_2H_5)_4NClO_4$ at 25°C and at −0.5 V *vs.* SCE at 50 cm of the height of mercury reservoir. 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)chromium(III) complex gave a six-step reduction wave when tetraethylammonium perchlorate was used as supporting electrolyte. The limiting currents of the first four reduction steps were each 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. Six reduction steps were also observed at 2.8°C and the ratio of the wave heights was nearly equal to the value at 25°C. The temperature coefficient of the limiting current at 25°C is about 0.8%/deg for each step. No anodic wave was observed at the potentials less positive than about +0.65 V, where the dissolution of mercury started. Upon the addition of free 2,2′-bipyridine to the solution containing 0.5 mM of the complex, the first four steps of the reduction wave were not affected in wave height and reduction potentials, but the wave heights of the fifth and the sixth step were increased. Free 2,2′-bipyridine gave a two-step reduction wave[2] at potentials corresponding nearly to the fifth and the sixth step of the polarogram of the complex. The results of log-plot analysis of the first three

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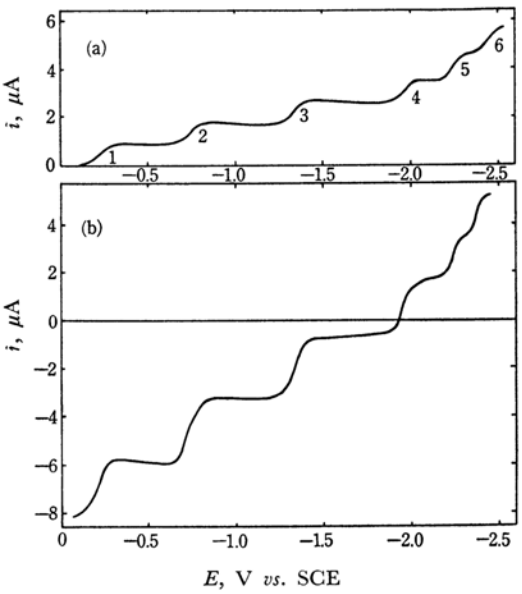

Fig. 1. (a) D.c. and (b) Kalousek polarograms with the solutions containing 0.5 mM $[Cr(bipy)_3](ClO_4)_3$ and 0.05 M $(C_2H_5)_4NClO_4$. E_2 potentials are set up at −2.1 V for curve (b).

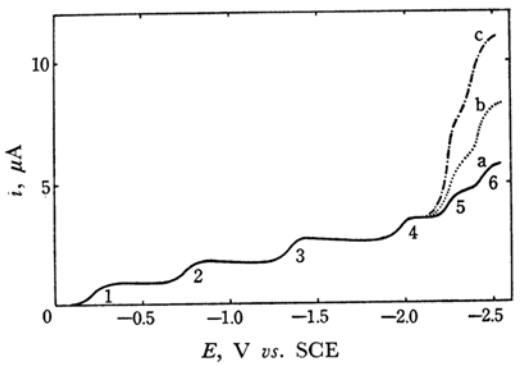

Fig. 2. D.c. polarograms of 0.5 mM $[Cr(bipy)_3](ClO_4)_3$ (a) in the absence and in the presence of (b) 0.028 M, (c) 0.139 M of water. Supporting electrolyte is 0.05 M $(C_2H_5)_4NClO_4$.

steps are given in Table 1. Upon the addition of a small concentration of water, the limiting currents of the fifth and the sixth step were increased, although no influence was found for the first four steps of the polarogram of the complex (see Fig. 2). The reduction wave of free 2,2′-bipyridine is also affected by the addition of a small concentration of water.[2] A. c. polarograms were recorded with solutions containing 0.5 mM of the complex. Six peaks were observed and their peak potentials were found to coincide with the half-wave potentials of the corresponding steps of the d. c. polarogram. The addition of 10 mM of free 2,2′-bipyridine increased the fifth and the sixth peak current, but gave almost no influence on the first four steps.

Table 1. Log-plot analysis for the first three steps of the reduction wave of the chromium(III)-bipyridine complex at 25°C

	$E_{1/2}$, V *vs.* SCE	Slope, mV
1st step	−0.221	61
2nd step	−1.741	58
3rd step	−1.327	51

Electrolytic solutions contain 0.5 mM $[Cr(bipy)_3](ClO_4)_3$, 10.0 mM 2,2′-bipyridine and 0.05 M $(C_2H_5)_4NClO_4$.

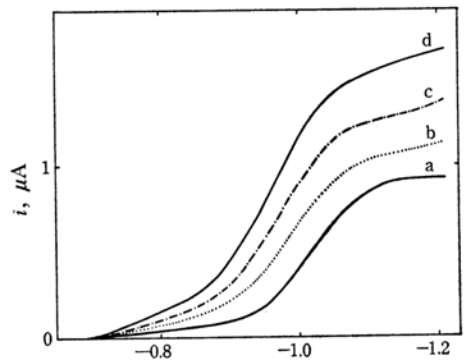

Fig. 3. The effect of 2,2′-bipyridine upon the reduction wave of 0.5 mM $[Cr(en)_3](ClO_4)_3$ containing 0.05 M $(C_2H_5)_4NClO_4$ as supporting electrolyte. 2,2′-bipyridine concentrations are (a) 0, (b) 0.5 mM, (c) 1.0 mM and (d) 3.0 mM.

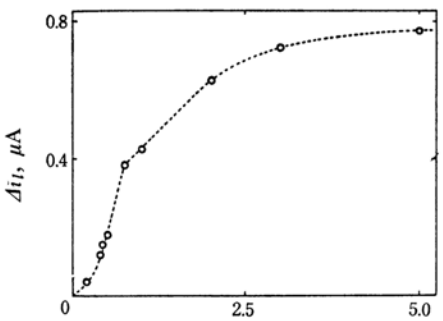

Fig. 4. Relation between the limiting current and the concentration of added 2,2′-bipyridine. Electrolytic solutions contain 0.5 mM $[Cr(en)_3](ClO_4)_3$, 0.05 M $(C_2H_5)_4NClO_4$ and 2,2′-bipyridine. Δi_l is the difference of the limiting current at −1.20 V in the presence and the absence of 2,2′-bipyridine.

The reversibilities of the first four steps were confirmed by the measurement of Kalousek polarograms, when the electrode potentials of the DME were set up at −0.5 V, −1.0 V, −1.6 V and −2.1 V, which are the potentials on the limiting currents of the first, the second, the third and the fourth

TABLE 2. THE RELATION BETWEEN THE LIMITING CURRENT OF THE CHROMIUM(III)-ETHYLENEDIAMINE COMPLEX AT −1.20 V AND THE HEIGHT OF MERCURY RESERVOIR IN THE PRESENCE OF 0.4 mM AND 5.0 mM OF 2,2′-BIPYRIDINE

(A) 0.4 mM 2,2′-bipyridine

h, cm	$\bar{i}_l$, μA	$\bar{i}_l°$, μA	$\Delta\bar{i}_l$, μA
45	1.14	0.91	0.23
50	1.18	0.95	0.23
55	1.21	0.99	0.22
60	1.26	1.03	0.23

(B) 5.0 mM 2,2′-bipyridine

h_{corr}, cm	i_l, μA	$i_l°$, μA	Δi_l, μA	$\sqrt{h_{corr}}$, $cm^{1/2}$	$\Delta i_l/\sqrt{h_{corr}}$, $\mu A/cm^{1/2}$
42.86	1.58	0.91	0.67	6.55	0.102
47.86	1.76	0.95	0.81	6.92	0.117
52.86	1.85	0.99	0.86	7.27	0.118
57.86	1.94	1.03	0.91	7.61	0.119

Electrolytic solutions contain 0.5 mM $[Cr(en)_3](ClO_4)_3$, 0.05 M $(C_2H_5)_4NClO_4$ and 2,2′-bipyridine. $i_l°$ is the limiting current of the complex in the absence of 2,2′-bipyridine at −1.20 V. $\Delta\bar{i}_l=\bar{i}_l-\bar{i}_l°$

step, respectively. A four-step oxidation wave was obtained, when the electrode potential was set up at −2.1 V (Fig. 1).

Tris(ethylenediamine)chromium(III) perchlorate gave a two-step reduction wave at −1.018 V and −1.650 V when tetraethylammonium perchlorate was used as supporting electrolyte. The ratio in wave height was 1 : 2 and the limiting current of each step was diffusion-controlled. Diffusion current constant, $I_d(=\bar{i}_d/m^{2/3}t_d^{1/6}C)$, for the first step was 1.86, which showed one-electron[1-4] reduction from chromium(III) to chromium(II). Log-plot analysis for the first step was not linear. As 2,2′-bipyridine was added to the solution containing $[Cr(en)_3](ClO_4)_3$ and $(C_2H_5)_4NClO_4$, the limiting current of the first step was increased as shown in Fig. 3. Although the limiting current of the first step was increased with increasing concentration of bipyridine at constant concentration of the complex, $\Delta\bar{i}_l$ (the difference of the limiting current at −1.2 V in the presence and the absence of free bipyridine) was not proportional to the concentration of bipyridine, but approached to the definite value (Fig. 4). The total limiting current of the first step never exceeded twice of the limiting current of the complex. The limiting current ($\Delta\bar{i}_l$) was proportional to the square root of the mercury pressure in the presence of excess bipyridine, whereas it was independent of the mercury pressure when the concentration of bipyridine was smaller than that of the complex (See Table 2). The addition of free anhydrous ethylenediamine to the solution containing the complex and 2,2′-bipyridine depressed the limiting current to the original wave height of the complex only. Kalousek polarograms of 0.5 mM tris(ethylenediamine)chromium-(III) which were obtained in the presence and the absence of 2,2′-bipyridine are given in Fig. 5.

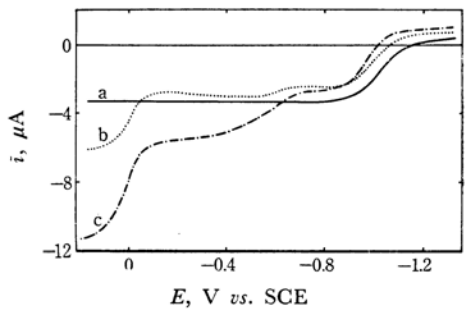

Fig. 5. Kalousek polarograms of 0.5 mM $[Cr(en)_3](ClO_4)_3$ (a) in the absence and in the presence of (b) 0.4 mM, (c) 5.0 mM 2,2′-bipyridine. Supporting electrolyte is 0.05 M $(C_2H_5)_4NClO_4$ and E_2 potentials are set up at −1.20 V.

When the electrode potential was set up at −1.2 V (the potential of the limiting current of the first step of the reduction wave), a one-step oxidation wave was observed in the absence of free bipyridine (curve a in Fig. 5), but two new steps appeared at about 0 V and −0.6 V in the presence of free bipyridine (curves b and c in Fig. 5). The limiting currents of two new oxidation waves were increased with increasing concentrations of bipyridine at the constant concentration of the complex.

Discussion

The limiting current of the first four steps of tris(2,2′-bipyridine)chromium(III) is concluded to be diffusion-controlled from the linear dependence of the wave height on the square root of the mercury pressure and on the complex concentrations and from the temperature coefficient of the limiting currents.[2] The diffusion current constant, $I_d(=\bar{i}_d/m^{2/3}t_d^{1/6}C)$, for the limiting current of the first step is 1.86, which is nearly equal to the value

for the one-electron reduction of various 2,2'-bipyridine complexes in acetonitrile.[1-4] The ratio of the wave heights of the first five steps is $1.00 : 1.1_0 : 1.1_0 : 1.0_7 : 1.8_7$. The fact that the wave heights of the first four steps of the complex are not influenced but those of the last two steps are by the addition of free 2,2'-bipyridine and a small concentration of water shows that the electrode processes of the first four steps and the latter two steps are different in nature. The log-plot analysis and Kalousek polarograms indicate that the electrode processes of the first four steps are reversible. From the same consideration as in the case with the reduction of the iron(II) complex[2] in addition to the fact that the reduction potential of free 2,2'-bipyridine is equal to the potential of the fifth and the sixth step of the reduction wave of the complex, the first four steps are concluded to be each due to the one-electron reduction of the chromium(III) complex itself and the latter two steps, the reduction of free bipyridine liberated from the complex. The first four steps are:

$$[Cr(bipy)_3]^{3+} \underset{-e}{\overset{e}{\rightleftharpoons}} [Cr(bipy)_3]^{2+} \underset{-e}{\overset{e}{\rightleftharpoons}} [Cr(bipy)_3]^{+} \underset{-e}{\overset{e}{\rightleftharpoons}} [Cr(bipy)_3] \underset{-e}{\overset{e}{\rightleftharpoons}} [Cr(bipy)_3]^{-} \quad (1)$$

A four-step oxidation wave obtained by Kalousek circuit (Fig. 1) clearly showed the formation of tris(2,2'-bipyridine)chromate anion, $[Cr(bipy)_3]^-$, at the electrode surface in the potential region of the fourth step of the reduction wave. Recently Herzog, Grimm and Waicenbauer[7] prepared $Li[Cr(bipy)_3]\cdot 4THF$ (THF: tetrahydrofuran). The preparations of $Na_2[Cr(bipy)_3]\cdot 7THF$, $Na_3[Cr(bipy)_3]\cdot 7THF$ and $Ca_3[Cr(bipy)_3]\cdot 7NH_3$ were also reported in their paper.[7] In acetonitrile solutions the wave height of the fifth step of the reduction wave is influenced by the addition of water and is larger than that of the first four steps, and the reduction potential of the fifth step coincides nearly to the reduction potential of free bipyridine. Therefore, the formation of stable bivalent or higher valent anions of tris(bipyridine)chromate at the electrode surface seems unlikely. In aqueous solutions some confusing results on the reduction of $[Cr(bipy)_3]^{3+}$ at the DME are obtained.[5,8,9] The result obtained in acetonitrile solution is similar to that obtained by Vlček, but in aqueous solutions only three reduction steps were observed and $[Cr(bipy)_3]$ is the lowest oxidation state.

The increase in wave height of the reduction of tris(ethylenediamine)chromium(III) to chromium(II) by the addition of 2,2'-bipyridine is explained as follows. The limiting current at -1.2 V is considered to be kinetic in nature in the presence of a small concentration of bipyridine from the result that the wave height ($\Delta\bar{\imath}_l$) is independent of the mercury pressure (Table 2). The fact that the reduction product of $[Cr(en)_3]^{3+}$ is substitution-labile suggests the occurrence of the following substitution reaction at the electrode surface (Eq. (3)).

$$[Cr(en)_3]^{3+} + e \rightarrow [Cr(en)_3]^{2+} \quad (2)$$

$$[Cr(en)_3]^{2+} + p\,bipy \rightleftarrows [Cr(en)_{3-p}(bipy)_p]^{2+} + p\,en \quad (3)$$

$$[Cr(en)_{3-p}(bipy)_p]^{2+} + e \rightarrow [Cr(en)_{3-p}(bipy)_p]^{+} \quad (4)$$

The increase in wave height is owing to the reduction of $[Cr(en)_{3-p}(bipy)_p]^{2+}$ (Eq. (4)), because the half-wave potentials of $[Cr(en)_{3-p}(bipy)_p]^{2+}$ is considered to be nearly equal to that of $[Cr(bipy)_3]^{2+}$ ($E_{1/2}=-0.741$ V as cited in Table 1) and is less negative than that of the first step of $[Cr(en)_3]^{3+}$ ($E_{1/2}=-1.018$ V). The appearance of the new oxidation steps on the Kalousek polarogram (curves b and c in Fig. 5) shows the oxidation of $[Cr(en)_{3-p}(bipy)_p]^{+}$ to higher oxidation states, which is the reduction product of $[Cr(en)_{3-p}(bipy)_p]^{2+}$ formed at -1.20 V. Half-wave potentials of two new steps of the oxidation wave are somewhat less negative than those of the corresponding steps in the case of $[Cr(bipy)_3]^{3+}$ as shown in Fig. 1,

$$[Cr(bipy)_3]^{+} \rightarrow [Cr(bipy)_3]^{2+} + e \quad (5)$$

$$[Cr(bipy)_3]^{2+} \rightarrow [Cr(bipy)_3]^{3+} + e \quad (6)$$

When the concentration of 2,2'-bipyridine added (C_{bipy}) was less than that of the complex, the plot of $\log\Delta\bar{\imath}_l$ *vs.* $\log C_{bipy}$ was linear and its slope was about 2. This seems to suggest that two bipyridine molecules are coordinated to the electroactive Cr(II) species (namely $p=2$ in Eq. (3)), though electroactive species is not $[Cr(en)(bipy)_2]^{2+}$ but $[Cr(bipy)_2(CH_3CN)_q]^{2+}$. In the case with the reduction of *trans*-$[Cr(NCS)_2(en)_2](SCN)$ in acetonitrile ($E_{1/2}$ is about -1.17 V), a similar phenomenon is also observed in the presence of 2,2'-bipyridine. The depression of wave height ($\Delta\bar{\imath}_l$) by the addition of free ethylenediamine shows that the rate of the backward reaction of reaction (3) is accelerated. If the above discussion is correct, this is another example of the electrode process followed by chemical reaction involving an electroactive species.[10-12]

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