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POLAROGRAPHY OF TRIS(2,2'-BIPYRIDINE)VANADIUM(0)

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Polarograms and cyclic voltammograms of tris(2,2'-bipyridine) vanadium(0) were taken in a DMF solution. They exhibited three one-electron reduction waves corresponding to VL_3^-/VL_3 (L=2,2'-bipyridine)-VL_3^{2-}/VL_3^- and VL_3^{3-}/VL_3^{2-} and two oxidation waves corresponding to VL_3/VL_3^+ and VL_3^+/VL_3^{2+}. The oxidation-reduction potential difference for VL_3^+ was anomalously small. This was explained by assuming diamagnetism of VL_3^+.

Several tris(2,2'-bipyridine)vanadium complexes in lower oxidation states have been prepared.[1,2] Their polarograms, however, have not yet apparently been reported, except for a reduction wave of $V(bipy)_3^{2+}$ to $V(bipy)_3^+$.[3] In this paper we report a reduction and an oxidation polarogram of tris(2,2'-bipyridine)vanadium(0) taken in an N,N-dimethylformamide (DMF) solution containing 0.2 M tetra-n-butylammonium perchlorate (TBAP).

Tris(2,2'-bipyridine)vanadium(0) is very sensitive to oxygen. It was prepared[1] and handled *in vacuo* and in a nitrogen atmosphere. It was identified by the elementary analysis.

Figure 1 shows a cathodic polarogram of 1.0 mM $V(bipy)_3$ solution. It exhibits five reduction waves with half-wave potentials of -1.55, -2.10, -2.23, -2.6 and -2.73 V vs. SCE. The wave-heights of two reduction waves at -1.55 and -2.23 V are identical when corrected for the mercury drop area. The wave at -2.73 V is of almost the same height with these waves when corrected for the ultimate current rise. The other two waves at -2.10 and -2.6 V are much lower than these. They may be attributable to reduction of free 2,2'-bipyridine molecules, because a polarogram of the latter substance obtained under the same conditions as mentioned above showed two reduction waves at -2.10 and -2.66 V.

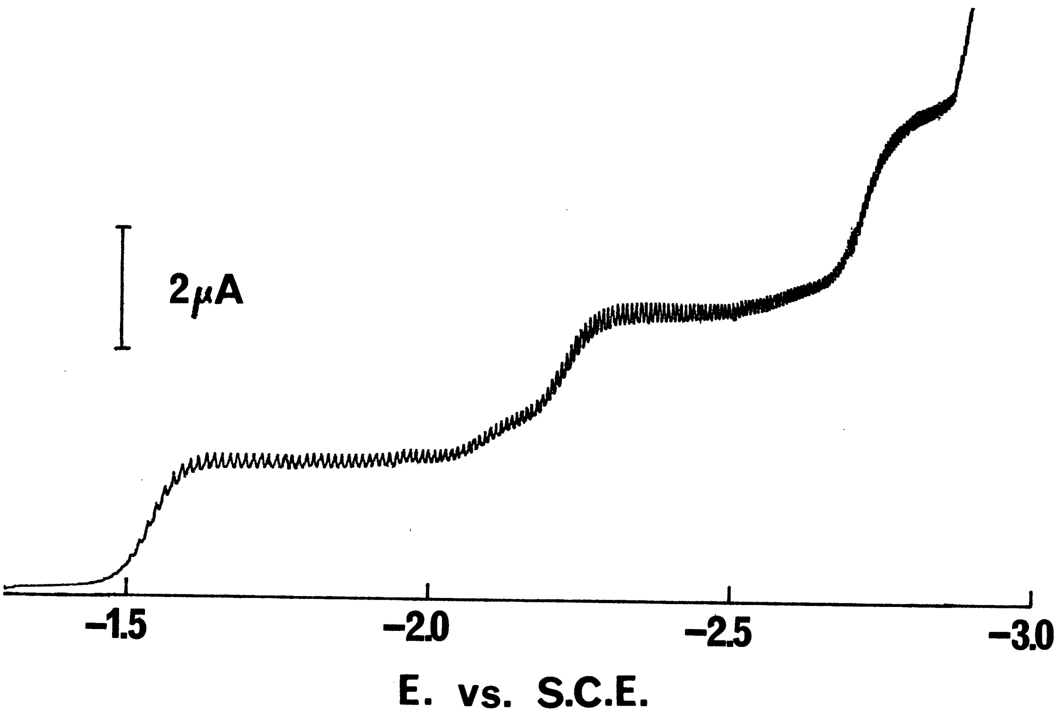

Fig. 1. Polarogram for reduction of 1.0 mM $V(bipy)_3$ in DMF containing 0.2 M TBAP.

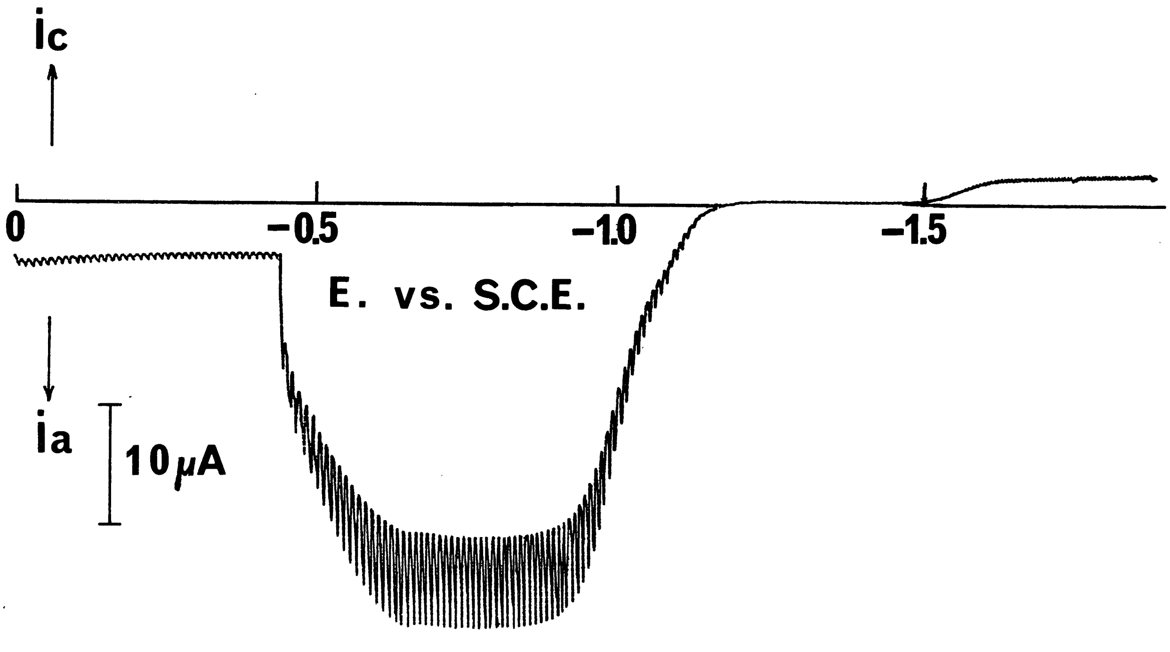

Fig. 2. Polarogram for oxidation of 1.0 mM $V(bipy)_3$ in DMF containing 0.2 M TBAP.

Figure 2 shows a polarogram in the cathodic-anodic polarization. The anodic wave has a large maximum falling abruptly at -0.44 V and a diffusion plateau at more positive potentials. The plateau height is twice the height of the reduction wave at -1.55 V. The potential at which the maximum current ends is approximately the zero-charge potential in this solution. Such behavior of the polarogram has already been observed in the anodic polarization of several hydrocarbon anion radicals.[4,5] The anodic maximum of this kind has rarely been reported for metal complexes. We have found the same maximum in the polarograms of the complexes of titanium, molybdenum and chromium. Both maxima in hydrocarbons and metal complexes may be considered to have a common origin. In view of these circumstances the anodic polarogram was obtained by cyclic voltammetry with a platinum working electrode. The voltammogram in Fig. 3 shows two oxidation waves partly overlapped. From their peak potentials the corresponding usual half-wave potentials were obtained to be -1.01 and -1.11 V vs. SCE. The reversibility criterion of the peak-potential separation and the peak-current ratio show that these waves are reversible one-electron waves. Considering the plateau height in Fig. 2, they may be attributed to the parent compound. Cyclic voltammograms for reduction of $V(bipy)_3$, on the other hand, show that waves at -1.55 and -2.23 V are also reversible one-elctron waves.

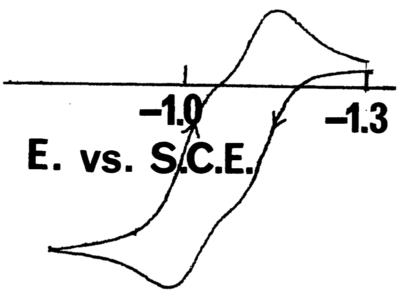

Fig. 3. Cyclic voltammogram for oxidation of 1.0 mM $V(bipy)_3$ in DMF containing 0.2 M TBAP.

The half-wave potentials of -1.01, -1.11, -1.55, -2.23 and -2.73 V can thus be assigned to the $V(bipy)_3^{2+}/V(bipy)_3^{+}$, $V(bipy)_3^{+}/V(bipy)_3$, $V(bipy)_3/V(bipy)_3^{-}$, $V(bipy)_3^{-}/V(bipy)_3^{2-}$ and $V(bipy)_3^{2-}/V(bipy)_3^{3-}$ redox couples respectively. Here we term the difference between the half-wave potentials of the oxidation and the reduction waves of a species in a particular oxidation state as the oxidation-reduction potential difference of that species and designate it by $\Delta E_{1/2}$. The $\Delta E_{1/2}$ values for the tris-bipyridine vanadium complexes are listed in table 1 together with those for the corresponding isoelectronic chromium complexes. The electronic configurations and the total spin numbers of tris(2,2'-bipyridine)chromium complexes are as follows: $Cr(bipy)_3^{3+}(t_{2g}^{3}, S = 3/2)$, $Cr(bipy)_3^{2+}(t_{2g}^{4}, S = 1)$, $Cr(bipy)_3^{+}(t_{2g}^{5}, S = 1/2)$, $Cr(bipy)_3(t_{2g}^{6}, S = 0)$ and $Cr(bipy)_3^{-}(t_{2g}^{6}e_g, S = 1/2)$.[6] Based on this fact, it may be reasonable to predict that the $\Delta E_{1/2}$ values for the d^4 and d^5 complexes are identical and the d^6 complex has a larger $\Delta E_{1/2}$ value compared with the former two, because the $\Delta E_{1/2}$ of the latter complex may possibly be contributed from the energy difference between the t_{2g} and e_g orbitals.[6] Table 1 shows that the predicted relation holds among the $\Delta E_{1/2}$ values for the chromium complexes. From this point of view the $\Delta E_{1/2}$ values of 0.10 V is anomalously small. An explanation of this anomaly is

Table 1 $\Delta E_{1/2}$ values for isoelecronic complexes of tris(2,2'-bipyridine)vanadium and chromium.

Nos. of d-electron		d^4	d^5	d^6	d^7
$\Delta E_{1/2}$ (V)	Cr[a)]	0.49	0.48	0.66	
	V	0.10	0.44	0.68	0.50

a) Obtained in a DMF solution containing 0.2 M TBAP.

as follows. It is known that Ti(bipy)$_3$(d^4, S = 0) is diamagnetic.[7)] The diamagnetism of this complex which is isoelectronic with V(bipy)$_3^+$ and Cr(bipy)$_3^{2+}$ has been considered to be caused by strong splitting of the t_{2g} orbital within the partly filled d-shell, $t_{2g} \longrightarrow e_g' + a$, with the e_g' orbital being the lowest. This large splitting has been interpreted by Orgel[8)] to be caused by strong π-type interaction of the e_g' orbital with antibonding ligand orbitals. As for the magnetism of vanadium complexes, on the other hand, the measurement of the magnetic susceptibility of V(bipy)$_3^+$ has not yet been successful and the methanolic solution of V(bipy)$_3$I does not exhibit ESR signals,[9)] while V(bipy)$_3^{2+}$ and V(bipy)$_3$ are known to be paramagnetic and to have total spin of 3/2 and 1/2 respectively.[9)] If the V(bipy)$_3^+$ ion in solution is assumed to be diamagnetic, the electronic configurations of V(bipy)$_3^{2+}$, V(bipy)$_3^+$ and V(bipy)$_3$ can be t_{2g}^3, $e_g'^4$ and $e_g'^4 a$ respectively. Then the small $\Delta E_{1/2}$ value for V(bipy)$_3^+$ may be explicable.

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6) This is not necessarily an e_g orbital but it may be a ligand orbital.

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