Polarographic Behaviour in Acetone of Complexes formed between the Bis(π-cyclopentadienyl)vanadium(IV) Group and some 1,1-Dithio-chelates

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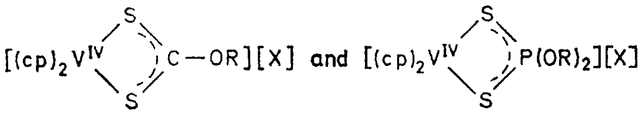
The polarographic behaviour of complexes formed between the bis(π-cyclopentadienyl)vanadium(IV) group and some *O*-alkyl dithiocarbonates and *OO'*-dialkyl dithiophosphates has been investigated in acetone. Each complex exhibits two well defined one-electron reduction waves, and in most cases further reduction waves. The wave at most positive potentials is associated with the reversible process $[(cp)_2V^{IV}L]^+ + e \rightleftharpoons [(cp)_2V^{III}L]^0$ (where L is an alkyl dithiocarbonate or dialkyl dithiophosphate). For L = methyl dithiocarbonate and dialkyl dithiophosphate, the neutral vanadium(III) complexes are prone to dissociation. Mercury is oxidized in the presence of released ligand providing an example of $\overrightarrow{E}\overleftarrow{C}E$ mechanisms.

AN ELECTROCHEMICAL investigation on a series of complexes between the bis(π-cyclopentadienyl)vanadium(IV) group and certain dialkyl dithiocarbamates[1] showed that they underwent a novel set of processes at a mercury electrode which could be described by the terminology $\overrightarrow{E}C_1\overleftarrow{E}C_2$ [where $\overrightarrow{E}$ represents a reduction of vanadium(IV) to vanadium(III), C_1 a subsequent chemical reaction in which co-ordinated dialkyl dithiocarbamate is released from the metal, $\overleftarrow{E}$ an oxidation of mercury(0) to form *NN*-dialkyldithiocarbamatomercury(I) and C_2 a chemical disproportionation equilibrium between mercury-(I) and -(II) dialkyl dithiocarbamates]. Here we report the results of a study on an analogous series of complexes with co-ordinated *O*-alkyl dithiocarbonates and *OO'*-dialkyl dithiophosphates.

The physical properties of these complexes[2,3] strongly suggest that they are of the forms



where cp represents a π-bonded cyclopentadienyl group, R an alkyl group, and X the tetraphenyl- or tetrafluoroborate anion. Under bonding schemes generally used for compounds containing $(cp)_2M$ groups,[4,5] a site is available for the addition of a further electron, thereby enabling the production of neutral vanadium(III) species of the types $[(cp)_2V^{III}(S_2P[OR]_2)]^0$ and $[(cp)_2V^{III}(S_2COR)]^0$. Any further reduction steps are expected to give rise to complex electrochemistry since the resulting products are predicted to be unstable.

The following abbreviations have been used in the text: cp, π-bonded cyclopentadienyl; axan, *O*-alkyl dithiocarbonate (or more commonly ' alkyl xanthate '); mxan, *O*-methyl dithiocarbonate; exan, *O*-ethyl dithiocarbonate; pxan, *O*-isopropyl dithiocarbonate; bxan, *O*-butyl dithiocarbonate; chxan, *O*-cyclohexyl dithiocarbonate; dmdtp, *OO'*-dimethyl dithiophosphate; dedtp, *OO'*-diethyl dithiophosphate; dcedtp, *OO'*-dichloroethyl dithiophosphate; dpdtp, *OO'*-di-isopropyl dithiophosphate; dbdtp, *OO'*-dibutyl dithiophosphate; dodtp, *OO'*-dioctyl dithiophosphate.

EXPERIMENTAL

Instrumentation.—Polarograms were recorded in acetone with Metrohm or PAR instrumentation as described elsewhere[1,6,7] using 0·1M-tetraethylammonium perchlorate as supporting electrolyte. The reference electrode was Ag/AgCl (0·1M-LiCl; acetone) and the auxiliary electrode was platinum wire.

All test solutions were thoroughly degassed with acetone-saturated argon (unless otherwise stated) and a continuous stream of argon was passed over solutions while measurements were being taken. Solutions were thermostatted to 20·0 ± 0·1 °C in a water-jacketted cell.

Preparations.—*Bis(π-cyclopentadienyl)*(O-*alkyl dithiocarbonato)vanadium*(IV) *Tetrafluoroborates and Bis-(π-cyclopentadienyl)*(OO'-*dialkyl dithiophosphato)vanadium*(IV) *Tetrafluoro- and Tetraphenyl-borates.* These complexes were prepared from $(cp)_2VCl_2$ and the appropriate potassium alkyl dithiocarbonate or *OO'*-dialkyl dithiophosphoric acid by the methods described elsewhere.[2,3]

RESULTS AND DISCUSSION

Polarographic Behaviour of Potassium O-*Alkyl Dithiocarbonates and Ammonium* OO'-*Dialkyl Dithiophosphates.*—A description of the polarography of the ligands is essential for a complete understanding of the electrochemistry of the vanadium(IV) complexes. All the alkyl dithiocarbonates and dialkyl dithiophosphates studied exhibited three oxidation waves. Interest in relation to the vanadium(IV) complexes lay in waves 1 and 2 which had respective half-wave potentials near −0·35 and +0·10 V *vs.* Ag/AgCl for the alkyl dithiocarbonates, and −0·15 and +0·15 V *vs.* Ag/AgCl for the dialkyl dithiophosphates. Because of the nature of electrode processes, $E_{\frac{1}{2}}$-values vary with concentration and ligand.[6,7]

The detailed electrochemistry of waves 1 and 2 is

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[1] A. M. Bond, A. T. Casey, and J. R. Thackeray, *Inorg. Chem.*, 1973, **12**, 887.

[2] A. T. Casey and J. R. Thackeray, *Austral. J. Chem.*, 1972, **25**, 2085.

[3] J. R. Thackeray, Ph.D. Thesis, University of Melbourne, 1973.

[4] C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, 1961, **15**, 1333.

[5] J. C. Green, M. L. H. Green, and C. K. Prout, *J.C.S. Chem. Comm.*, 1972, 421.

[6] A. M. Bond, A. T. Casey, and J. R. Thackeray, *J. Electrochem. Soc.*, 1973, **120**, 1502.

[7] A. M. Bond, A. T. Casey, and J. R. Thackeray, *J. Electroanalyt. Chem.*, 1973, **48**, 71.

described elsewhere.[6,7] The waves are associated with the processes

$$2\mathrm{Hg}^0 + 6\mathrm{axan}^- \rightleftharpoons 2\mathrm{Hg}^{\mathrm{II}}(\mathrm{axan})_3^- + 4e \text{ [designated } (\overset{\leftarrow}{\mathrm{E}}_1)]$$

for wave 1, and

$$2\mathrm{Hg}^{\mathrm{II}}(\mathrm{axan})_3^- + \mathrm{Hg}^0 \rightleftharpoons 3\mathrm{Hg}^{\mathrm{II}}(\mathrm{axan})_2 + 2e^- \text{ [designated } (\overset{\leftarrow}{\mathrm{E}}_2)]$$

for wave 2. Dialkyl dithiophosphate ligands undergo similar processes at the d.m.e.

Half-wave potentials for alkyl dithiocarbonate and dialkyl dithiophosphate complexes

Compound	$E_{\frac{1}{2}}$ (wave 1)/V (*vs.* Ag/AgCl)	$(E_{1/4} - E_{3/4})$/V	$E_{\frac{1}{2}}$ (wave 2)/V (*vs.* Ag/AgCl)	$(E_{1/4} - E_{3/4})$/V	$E_{\frac{1}{2}}$ (wave 3)/V (*vs.* Ag/AgCl)
$[(\mathrm{cp})_2\mathrm{V}(\mathrm{mxan})][\mathrm{BF}_4]$	−0·243	0·060	−1·387	0·080	−1·9
$[(\mathrm{cp})_2\mathrm{V}(\mathrm{exan})][\mathrm{BF}_4]$	−0·254	0·060	−1·380	0·068	−1·8
$[(\mathrm{cp})_2\mathrm{V}(\mathrm{pxan})][\mathrm{BF}_4]$	−0·274	0·060	−1·445	0·078	−1·9
$[(\mathrm{cp})_2\mathrm{V}(\mathrm{bxan})][\mathrm{BF}_4]$	−0·288	0·062	−1·436	0·076	−1·9
$[(\mathrm{cp})_2\mathrm{V}(\mathrm{chxan})][\mathrm{BF}_4]$	−0·300	0·060	−1·438	0·076	−1·9
$[(\mathrm{cp})_2\mathrm{V}(\mathrm{dmdtp})][\mathrm{BF}_4]$	−0·082	0·064	−0·63	0·087	
$[(\mathrm{cp})_2\mathrm{V}(\mathrm{dedtp})][\mathrm{Ph}_4\mathrm{B})$	−0·132	0·066	−0·70	0·105	*a*
$[(\mathrm{cp})_2\mathrm{V}(\mathrm{dcedtp})][\mathrm{Ph}_4\mathrm{B}]$	−0·060	0·067	−0·64	0·090	*a*
$[(\mathrm{cp})_2\mathrm{V}(\mathrm{dpdtp})][\mathrm{Ph}_4\mathrm{B}]$	−0·124	0·066	−0·67	0·090	*a*
$[(\mathrm{cp})_2\mathrm{V}(\mathrm{dbdtp})][\mathrm{Ph}_4\mathrm{B}]$	−0·122	0·068	−0·63	0·084	*a*
$[(\mathrm{cp})_2\mathrm{V}(\mathrm{dodtp})][\mathrm{Ph}_4\mathrm{B}]$	−0·104	0·068	−0·66	0·072	*a*

[a] Further wave(s) at more negative potentials were poorly defined.

*Polarographic Behaviour of Bis(π-cyclopentadienyl)(O-alkyl dithiocarbonato)vanadium(*IV*) Tetrafluoroborates.*— Each of the $[(\mathrm{cp})_2\mathrm{V}(\mathrm{axan})][\mathrm{BF}_4]$ complexes exhibited two one-electron reduction waves and a third wave near the cathodic limit (see Table and Figure 1). Wave 1, the wave at most positive potentials, was diffusion controlled over the concentration range *ca.* 10^{-3} to 10^{-4}M. For all complexes the half-wave potentials of this wave remained independent of concentration, and the diffusion currents were directly proportional to concentration over the above range. Plots of $\log[(i_d - i)/i]$ *vs.* potential were all linear over the range ±1 log unit and showed the Nernstian slope expected of waves from reversible one-electron reduction steps.

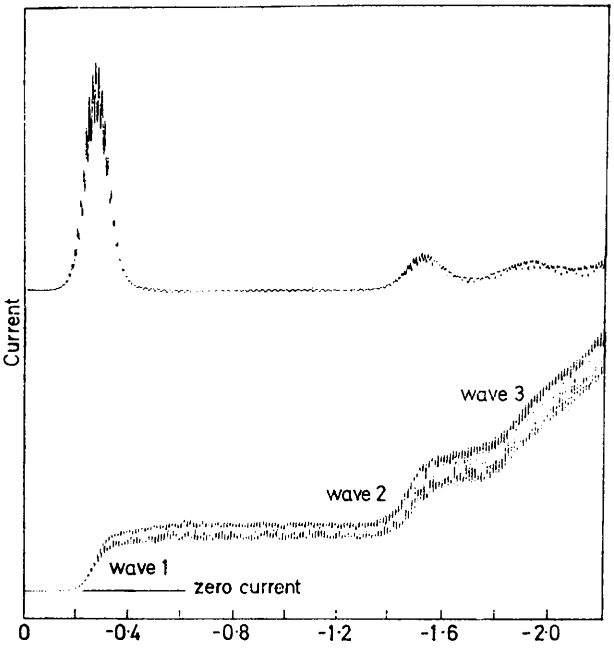

FIGURE 1 The DC and AC polarogram (500 Hz, 10 mV p-p, in phase component) of $[(\mathrm{cp})_2\mathrm{V}(\mathrm{pxan})][\mathrm{BF}_4]$

In AC polarograms, using conventional or short controlled-drop times, wave 1 had half-widths of 88 ± 2 mV at 500 Hz and its peak potential coincided exactly with the DC half-wave potential. The heterogeneous charge-transfer rate constant is therefore very large for this reduction step.

Wave 2 was more drawn out than wave 1 for all the complexes. Its associated $(E_{1/4} - E_{3/4})$ value was always somewhat larger than that expected of a reversible one-electron process (see Table), but the limiting current of this wave, for any one complex, was almost identical to the diffusion current of wave 1 for the same complex. In the AC sense, wave 2 had a half-width considerably greater than that expected for a reversible one-electron diffusion-controlled process and its peak potential was substantially more negative than the DC half-wave potential. As expected for a non-diffusion controlled AC reduction, wave 2 had a low peak current relative to that obtained from the reversible one-electron reduction (wave 1).

Wave 3 was also drawn out in the DC sense, but occurred too close to the cathodic limit for characterization. In AC polarograms it appeared as a very broad wave having a considerably lower peak current than the reversible wave 1 (see Figure 1).

Unless molecular oxygen was removed to an extent below that polarographically detectable, a deviation in the limiting current region of wave 1 (*ca.* −0·4 V) was seen. When oxygen was allowed to enter the system slowly, DC wave 1 was replaced by an extremely complex wave whose limiting current was almost exactly double the original diffusion current (*i.e.* equal in magnitude to the total current height of wave 1 plus wave 2 in the absence of oxygen). Waves 2 and 3 disappeared and a wave due to the reduction of oxygen was observed near −0·7 V.

In AC polarograms the current decreased markedly at the peak potential of wave 1 in the presence of oxygen and a new wave was clearly evident near —0·4 V (see Figure 2). When test solutions were repurged of oxygen, polarograms reverted to their normal behaviour. The addition of free axan anion to a solution of its corresponding complex also caused the deviation in wave 1 to grow substantially in the DC polarogram and a new wave was seen near +0·1 V. Wave 1 now had an anodic current, which was not evident in polarograms of the pure complexes even in the presence of oxygen. A detailed description of the electrode process was gained from AC measurements, where the addition of free axan ligand introduced a new wave near +0·1 V and a wave whose peak potential and shape coincided exactly with the new wave obtained near —0·4 V by introducing oxygen into the system. Furthermore, the addition of free ligand to a non-deoxygenated solution had the effect of increasing the magnitude of the alternating current near —0·4 V. Thus the anomalous polarographic behaviour of the complexes in the presence of oxygen may be explained by the oxygen-catalysed release of axan anions subsequent to the initial reduction. The AC peak height of wave 1 decreased in the presence of oxygen despite the large increase seen in the corresponding limiting current region of the DC polarogram. This is presumably because the AC processes are no longer reversible in the presence of oxygen. The lack of a DC anodic current at potentials more positive than the first reduction wave proves that free axan anions are only generated by the electrode processes and are not present in solution as impurity.

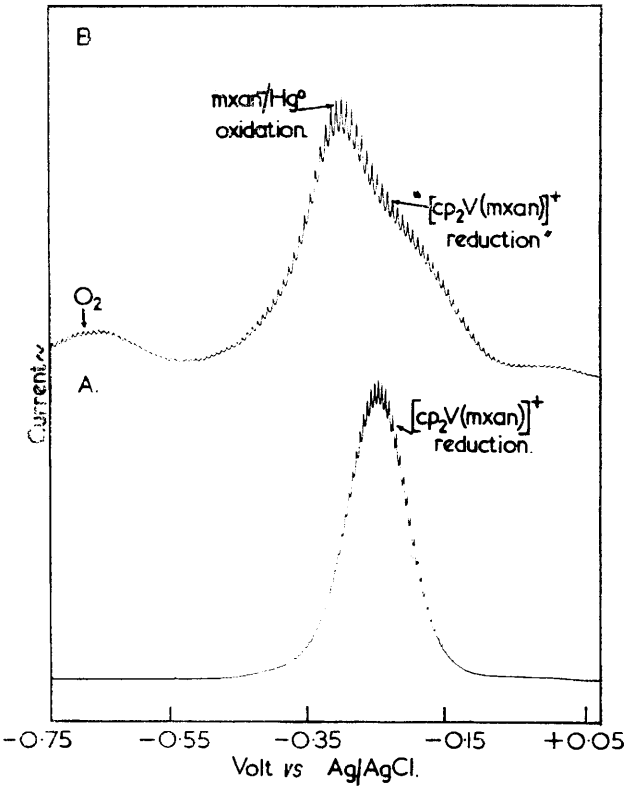

FIGURE 2 The AC polarogram of $[(cp)_2V(mxan)][BF_4]$ in the absence of oxygen (A) and in its presence (B) (50 Hz, 10 mV, r.m.s., total alternating current)

The general mechanism for the electrode processes associated with the first reduction step may now be written,

$$[(cp)_2V^{IV}(axan)]^+ + e \rightleftharpoons [(cp)_2V^{III}(axan)]^0 \qquad (\overrightarrow{E})$$

$$[(cp)_2V^{III}(axan)]^0 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} `[(cp)_2V^{III}]' + axan^- \qquad (C)$$

$$6axan^- + 2Hg^0 \rightleftharpoons 2Hg^{II}(axan)_3^- + 4e \qquad (\overleftarrow{E}_1)$$

where k_f and k_b are the forward and backward rate constants for step (C).

In the complete absence of oxygen the process is adequately described solely by step $\overrightarrow{E}$ for all but the methyl derivative (see later). The great enhancement of step $\overleftarrow{E}_1$ in the presence of oxygen is readily explicable in terms of the chemistry of vanadium. As a typical class '*a*' metal[8] it generally forms its most stable complexes with ligands which co-ordinate through donor atoms such as oxygen and nitrogen. The isolation and stability of the complexes studied here is presumably due to the π-bonded cyclopentadienyl groups which apparently bestow upon the vanadium atom properties more characteristic of latter members of the transition-metal series. Once the metal is reduced to vanadium(III) however, the complexes become most susceptible to the presence of oxygen (the corresponding $[(cp)_2Ti^{III}(axan)]^0$ complexes are very oxygen-sensitive)[9] and the resulting formation of oxovanadium-(IV) and/or -(V) species could easily initiate the release of the axan anion. The limiting current of the complex wave system between —0·1 and —0·5 V, in the DC polarograms from solutions containing oxygen, is close to double the diffusion current from step $\overrightarrow{E}$ in the absence of oxygen. In addition to steps $\overrightarrow{E}$ and $\overleftarrow{E}_1$, any oxovanadium species generated in the presence of oxygen may also undergo reduction at (or more positive to) these potentials and thereby add to the limiting current. Since step $\overleftarrow{E}_1$ has ceased by —0·4 V, the height of the wave near —0·5 V is consistent with all the vanadium(III) complexes produced reacting with oxygen to give oxovanadium species, and all these species undergoing a further one-electron reduction step. Waves 2 and 3 are no longer evident because the species causing them are not present in solutions containing oxygen. Slight evidence of the $\overleftarrow{E}$ step occurring in some polarograms where there was no polarographically detectable oxygen indicates that the $[(cp)_2V^{III}(axan)]^0$ complexes are extremely susceptible to even minute traces of oxygen. Thus like the corresponding dialkyl dithiocarbamate complexes,[1] these

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[8] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.

[9] R. S. P. Coutts, P. C. Wailes, and J. V. Kingston, *Austral. J. Chem.*, 1970, **23**, 469.

complexes can provide an example of a novel oxygen-catalysed $\overrightarrow{\mathrm{E}}\mathrm{C}\overleftarrow{\mathrm{E}}$ mechanism.

For reasons given previously,[1] the first electron uptake is expected to be associated with the vanadium atom, and therefore should produce neutral vanadium(III) complexes. It is difficult to discern whether the electron of the second reduction step enters an orbital primarily ligand in nature or one associated fundamentally with the vanadium atom. However the species resulting from this reduction must be unstable and presumably undergoes subsequent chemical reactions, since wave 2 is non-reversible. Wave 3 has a much lower limiting current than waves 1 and 2 and probably arises from a reduction step involving a fragmentation product from previous processes.

Polarographic Behaviour of Bis(π-*cyclopentadienyl*)-(OO′-*dialkyl dithiophosphato*)*vanadium*(IV) *Salts*.—Two main waves were obtained from polarograms of these complexes and in all cases except for the $[(\mathrm{cp})_2\mathrm{V}(\mathrm{dmdtp})][\mathrm{BF}_4]$ complex, further electrode processes were seen at more negative potentials (see Table and Figure 3). The half-wave potential of wave 1 was independent of concentration, while its limiting current was diffusion controlled and linearly dependent on concentration over the range 10^{-3}—10^{-4}M. Plots of $\log[(i_\mathrm{d} - i)/i]$ *vs.* potential were close to linear, but had gradients slightly greater than the Nernstian slope expected of waves from reversible one-electron reduction steps.

AC polarograms were very complex in the vicinity of wave 1. At low frequencies there appeared to be only one asymmetric wave near −0·1 V (having a half-height width near 100 mV). As the frequency was increased the wave became more asymmetric on the negative potential side, until at 300 Hz it was obvious that there were two overlapping waves present (see Figure 4).

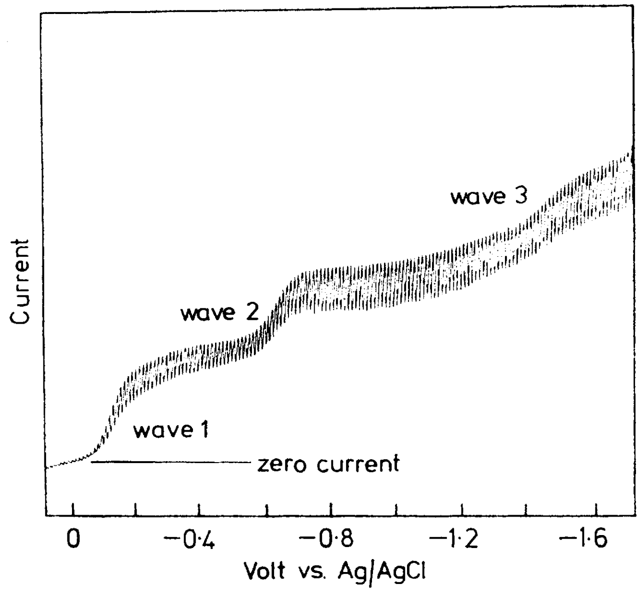

FIGURE 3 The DC polarogram of $[(\mathrm{cp})_2\mathrm{V}(\mathrm{dodtp})][\mathrm{Ph}_4\mathrm{B}]$

Free dadtp anions gave two waves in this potential region. The first occurred at more positive potentials than wave 1 ($\overleftarrow{\mathrm{E}}_2$) and the second at slightly more negative ($\overleftarrow{\mathrm{E}}_1$). The asymmetry on the cathodic side of AC wave 1 is due to the release of free dadtp anions subsequent to the reduction of vanadium(IV) to vanadium(III), and the electrode process is described by the $\overrightarrow{\mathrm{E}}\mathrm{C}\overleftarrow{\mathrm{E}}$ mechanism given previously for the alkyl dithiocarbonate complexes.

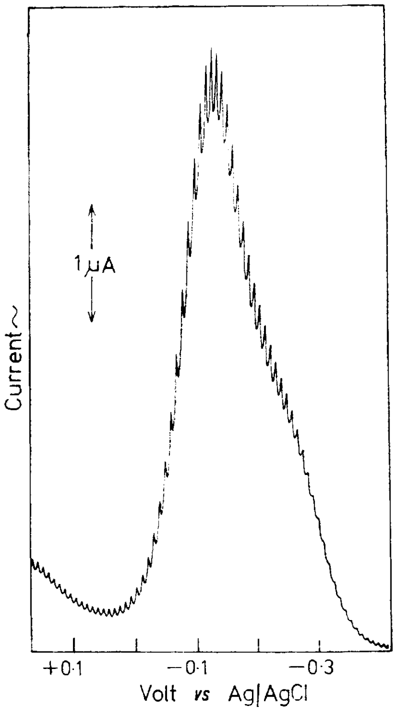

FIGURE 4 The AC polarogram of $[(\mathrm{cp})_2\mathrm{V}(\mathrm{dedtp})][\mathrm{Ph}_4\mathrm{B}]$ (300 Hz, 10 mV, p-p, in phase component)

The $\overrightarrow{\mathrm{E}}\mathrm{C}\overleftarrow{\mathrm{E}}$ mechanism is clearly evident for the $[(\mathrm{cp})_2\mathrm{V}(\mathrm{dadtp})][\mathrm{X}]$ complexes even in the absence of oxygen. AC peak potentials of wave 1 from the reduction of vanadium(IV) and wave 1 from free dadtp anions are both frequency dependent and sufficiently well separated at high frequencies to enable ready detection of both waves. The addition of free dadtp anions to a solution of the corresponding $[(\mathrm{cp})_2\mathrm{V}(\mathrm{dadtp})][\mathrm{Ph}_4\mathrm{B}]$ complex caused the wave on the cathodic side of complex wave 1 to grow. When oxygen was allowed to enter test solutions the $\overrightarrow{\mathrm{E}}\mathrm{C}\overleftarrow{\mathrm{E}}$ mechanism was catalysed substantially, as evidenced by the nature of the AC polarography.

The presence of an $\overrightarrow{\mathrm{E}}\mathrm{C}\overleftarrow{\mathrm{E}}$ mechanism was not readily discernible from the shape of the DC wave arising from the reduction of vanadium(IV) since the half-wave potential of this wave was too close to that of the free ligand wave 1. However, except for the $[(\mathrm{cp})_2\mathrm{V}(\mathrm{dmdtp})][\mathrm{BF}_4]$ complex, the height of wave 1 was always significantly greater than that of wave 2. This is expected for the $\overrightarrow{E}C\overleftarrow{E}$ mechanism because the C_1 dissociation step

$$[(cp)_2V^{III}(dadtp)]^0 \xrightarrow{k_F} \text{`}[(cp)_2V]\text{'} + dadtp^-$$

would lower the concentration of the neutral vanadium(III) species present at the electrode surface, and it is this species which is presumably responsible for wave 2. A further wave (wave 3) was seen at more negative potentials for most complexes and is probably associated with the dissociation product ' $[(cp)_2V^{III}]$.' As expected for a proposed mechanism of this type, the total height of waves 2 and 3 is equal to that of wave 1. Furthermore, the limiting currents of these waves are both drop-time dependent. In AC polarograms, waves 2 and 3 are very broad and have low peak currents typical of non-diffusion controlled processes. It is therefore concluded that they arise from kinetically controlled processes.

In the presence of oxygen DC wave 1 doubles in height and no processes corresponding to waves 2 and 3 are discernible. Clearly a similar mechanism to that obtained from the alkyl dithiocarbonate complexes in the presence of oxygen is also operable here.

The much greater instability of the $[(cp)_2V^{III}(dadtp)]^0$ complexes as compared to the corresponding dialkyl dithiocarbamate and alkyl dithiocarbonate series is consistent with the behaviour of the original vanadium(IV) complexes. The $[(cp)_2V^{IV}(dadtp)][X]$ complexes are unstable in the atmosphere and revert to brown oils unless stored under argon, whereas the analogous series with the other two sets of ligands are quite stable, even to prolonged exposure to the atmosphere.

Cyclic Voltammetry.—The applicability of this technique to ECE-type mechanisms has been well illustrated by Feldberg and Jeftic.[10] Samples of voltammograms obtained at a J-tube mercury electrode are shown in Figure 5. Figure 5A indicates that some dissociation of mxan ligand from the $(cp)_2V^{III}$ group occurs subsequent to the initial reduction even in the absence of oxygen, since the wave is considerably drawn out on the cathodic sweep and the separation of peak potentials is over 100 mV. In contrast, the $[(cp)_2V(bxan)]^+$ cation yields a cyclic voltammogram typical of that expected from a reversible system (see Figure 5C). The separation between anodic and cathodic peak potentials is 56 mV and there is no evidence of any dissociation. The dissociation of the $[(cp)_2V^{III}(mxan)]^0$ species was more evident in the cyclic voltammetry than the DC polarography. However the shape and nature of the DC wave 1 is also consistent with the cyclic voltammetry, as it, in fact, showed a slight deviation near —0·4 V for the $[(cp)_2V^{IV}(mxan)]^+$ cation, even after stringent precautions had been taken to remove oxygen (see Figure 2). No such effect was seen for the butyl derivative. The increase in stability of $[(cp)_2V^{III}(axan)]^0$ species in going from mxan to bxan may be attributable to increased inductive effects. Similar observations were made for the analogous dithiocarbamato-complexes.[1]

The addition of K(mxan) to a solution of the $[(cp)_2V(mxan)]^+$ complex caused a slight increase in the difference between cathodic and anodic peak potentials, and produced an anodic current at potentials more positive than the initial reduction ($\overrightarrow{E}$) (see Figure 5B). When oxygen was allowed to enter slowly the $\overrightarrow{E}C\overleftarrow{E}$ mechanism became clearly evident (see Figure 5D). The reduction wave from step ($\overrightarrow{E}$) gradually diminished in height and the reoxidation was barely discernible on anodic sweeps. After the first sweep the oxidation wave from step ($\overleftarrow{E}$) was of comparable height to that from step ($\overrightarrow{E}$) on cathodic sweeps.

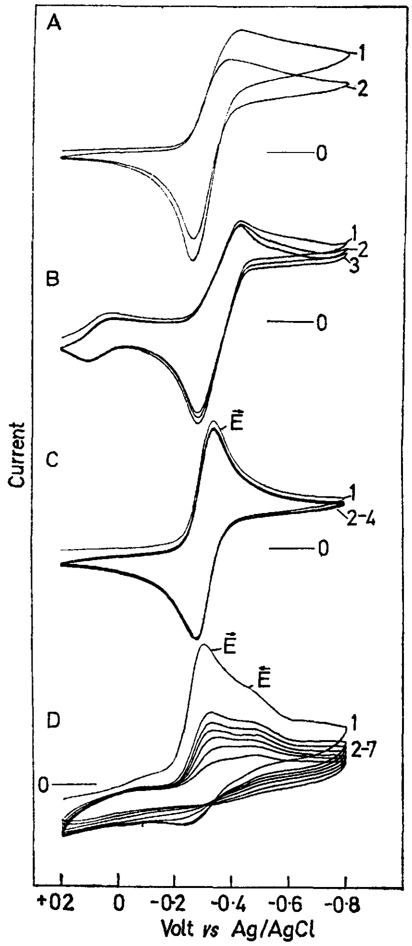

FIGURE 5 Cyclic voltammograms of $[(cp)_2V(axan)][BF_4]$ complexes at a J-tube mercury electrode. Successive sweeps are numbered on the right of each voltammogram and zero current is marked in each case. (A) $[(cp)_2V(mxan)][BF_4]$ in the absence of oxygen. Scan rate 50 mV/s. (B) $[(cp)_2V(mxan)][BF_4]$ + K(mxan). Scan rate 50 mV/s. (C) $[(cp)_2V(bxan)][BF_4]$ in the absence of oxygen. Scan rate 200 mV/s. (D) $[(cp)_2V(bxan)][BF_4]$ in the presence of oxygen.

A cyclic voltammogram from $[(cp)_2V(dpdtp)][Ph_4B]$ is shown in Figure 6. The separation of the peaks together with their width show that an $\overrightarrow{E}C\overleftarrow{E}$ mechanism is occurring even in the absence of oxygen.

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[10] S. W. Feldberg and L. Jeftic, *J. Phys. Chem.*, 1972, **76**, 2439.

Linear Sweep and Cyclic Voltammetry at a Platinum Electrode.—Linear-sweep voltammograms of the complexes could be recorded quite successfully at a platinum electrode. For the $[(cp)_2V(axan)][BF_4]$ series the first reduction step was reversible for $[(cp)_2V(bxan)][BF_4]$, but not for $[(cp)_2V(mxan)][BF_4]$ or the $[(cp)_2V(dadtp)][Ph_4B]$ series.

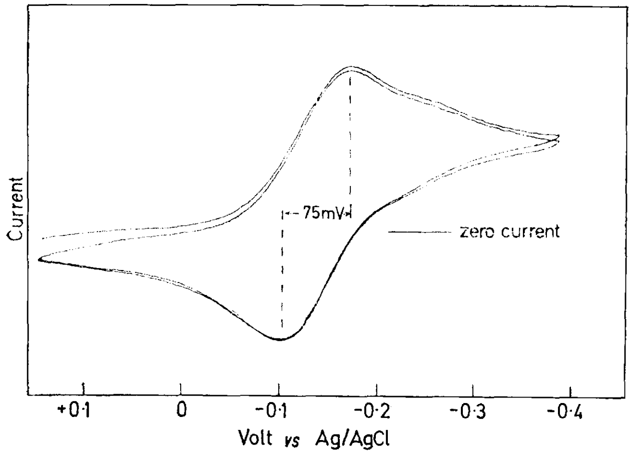

FIGURE 6 The cyclic voltammogram of $[(cp)_2V(dpdtp)][Ph_4B]$ at a J-tube mercury electrode. Scan rate = 50 mV/s

Equivalent observations were made with cyclic voltammograms. Where systems were exhibiting kinetic complications, larger separations were obtained between anodic and cathodic peak potentials than theoretically predicted for Nernstian behaviour and cathodic and anodic peak heights were not equal. The cathodic peak potential from the $[(cp)_2V(bxan)][BF_4]$ complex, for example, was 0·030 V more negative than the half-wave potential (as expected for a reversible system [11]), but was somewhat more negative for the $[(cp)_2V(mxan)][BF_4]$ complex. Finally, the lack of a wave corresponding to step $(\overleftarrow{\mathrm{E}})$ provides further evidence for the proposed mechanism, since the presence of mercury is required for processes $(\overleftarrow{\mathrm{E}_1})$ and $(\overleftarrow{\mathrm{E}_2})$. Studies at platinum electrodes are therefore compatible with the proposed mechanisms.

CONCLUSIONS

The present work has shown conclusively that, as predicted from theoretical considerations, a reversible one-electron charge transfer formally involving the reaction $[(cp)_2V^{IV}L]^+ \rightleftharpoons [(cp)_2V^{III}L]^0$ is a characteristic electrode process of complexes containing the $(cp)_2V^{IV}$ grouping co-ordinated by a dithio-chelate. Furthermore, it has been shown that the product of this electrode process, $[(cp)_2V^{III}L]^0$, has varying degrees of stability depending on the dithio-chelate L, and is always oxygen sensitive. The observed polarographic behaviour is entirely consistent with the known chemical and physical properties of the compounds.

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[11] P. Delahay, 'New Instrumental Methods in Electrochemistry,' Interscience, New York, 1954, p. 115.