Cp_2HfI_2, 37260-85-8; Cp_2TiPh_2, 1273-09-2; HI, 10034-85-2; Br_2, 7726-95-6.

Acknowledgments. We are grateful to Professor R. J. H. Clark of The University College, London, for reading the manuscript and for his helpful comments. We also thank Mrs. Henique and Mrs. Simmons for their assistance in carrying out the infrared and Raman measurements. A scholarship from the French Government to R. F. is gratefully acknowledged.

Contribution from the Inorganic Chemistry Department,
University of Melbourne, Parkville, Victoria, 3052, Australia

Polarographic Behavior of Bis(π-cyclopentadienyl)-*N*,*N*-dialkyldithiocarbamatovanadium(IV) Tetraphenylborates in Acetone. An Example of an $\overrightarrow{\mathrm{E}}\mathrm{C}\overleftarrow{\mathrm{E}}\mathrm{C}$ Mechanism

A. M. BOND,* A. T. CASEY, and J. R. THACKERAY

Received July 24, 1972

Bis(π-cyclopentadienyl)-*N*,*N*-dialkyldithiocarbamatovanadium(IV) tetraphenylborates exhibit two one-electron polarographic reduction waves in the potential range +0.75 to −2.2 V relative to a Ag–AgCl(acetone) reference electrode. The first reduction (at $\sim$−0.4 V) is fully reversible. It is believed that its associated electron is accommodated in a nonbonding orbital of the vanadium atom. The neutral vanadium(III) complexes resulting from this reduction are susceptible to dissociation, releasing free dialkyldithiocarbamate anions—a process which is greatly enhanced in the presence of oxygen. A study of sodium *N*,*N*-dialkyldithiocarbamates has shown that Hg(0) is oxidized to Hg(I) in the presence of free dialkyldithiocarbamate anions, and since this process occurs at $\sim$−0.5 V, a novel example of an $\overrightarrow{\mathrm{E}}\mathrm{C}\overleftarrow{\mathrm{E}}$ mechanism results. The terminology $\overrightarrow{\mathrm{E}}\mathrm{C}_1\overleftarrow{\mathrm{E}}\mathrm{C}_2$ has been used here to describe the following processes associated with the initial reduction step

$$[(cp)_2V^{IV}(dAdtc)]^+ + e \rightleftarrows [(cp)_2V^{III}(dAdtc)]^0 \qquad (\overrightarrow{\mathrm{E}})$$

$$[(cp)_2V^{III}(dAdtc)]^0 \underset{k_b}{\overset{k_f}{\rightleftarrows}} \text{“}[(cp)_2V^{III}]\text{”} + dAdtc^- \qquad (C_1)$$

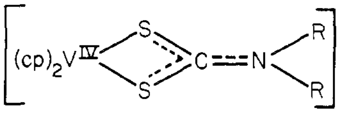
$$dAdtc^- + Hg^0 \rightleftarrows Hg^I(dAdtc) + e^- \qquad (\overleftarrow{\mathrm{E}})$$

$$2Hg^I(dAdtc) \rightleftarrows Hg^{II}(dAdtc)_2 + Hg^0 \qquad (C_2)$$

The second electrode process is not reversible. The system has been investigated by both dc and ac polarography, cyclic and linear sweep voltammetry, and controlled-potential electrolysis.

Introduction

Recently a number of air-stable complexes between the bis(π-cyclopentadienyl)vanadium(IV) moiety and some dialkyldithiocarbamates have been synthesized and characterized in this laboratory.[1] The physical properties of these compounds strongly suggest that they are of the form



where R is hydrogen or an alkyl group and X is either the tetraphenylborate or the tetrafluoroborate anion.

The suggested structure of the cationic species is shown in Figure 1. The vanadium atom is approximately tetrahedrally coordinated by two π-cyclopentadienyl groups and the two sulfur atoms of the dialkyldithiocarbamate, and it is predicted that its unpaired electron resides in a nonbonding orbital directed between the two sulfur atoms.[2] Epr data collected on the corresponding complexes between the $(cp)_2V^{IV}$ moiety and some dialkyl dithiophosphates[3] have shown conclusively that the vanadium–sulfur bonds are significantly covalent and that the unpaired electron does indeed occupy an orbital of the predicted type.

In view of the recent interest shown in the polarographic behavior of transition metal–dithio chelate complexes[4–7] and because of the uniqueness of stable complexes between early members of the transition series and dithio chelates, the above system seemed to warrant an electrochemical investigation. Indeed, it can be readily appreciated that the metal atom of these compounds is most favorably disposed toward reduction since it has a d^1 configuration, is involved in a cationic species, and has a partly filled nonbonding orbital as its lowest lying incompletely occupied energy level.

Since the compounds were completely insoluble in water, acetone was chosen as solvent. The complexes are moderately soluble in this solvent and there appears to be no solvolysis. Preliminary investigations on free dialkyldithiocarbamate anions showed an oxidation wave at $\sim$−0.5 V relative to Ag-AgCl, while a reduction wave at $\sim$−0.4 V relative to the same electrode was obtained from the complexes. It is clear that if any dissociation of dialkyldithiocarbamate ligands from the complexes occurs as a result of their initial reduction, then

---

(1) A. T. Casey and J. R. Thackeray, *Aust. J. Chem.*, **25**, 2085 (1972).

(2) C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, **15**, 1333 (1961).

(3) A. T. Casey and J. R. Thackeray, submitted for publication in *Aust. J. Chem.*

(4) D. C. Olson, V. P. Mayweg, and G. N. Schrauzer, *J. Amer. Chem. Soc.*, **88**, 4876 (1966), and references therein.

(5) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

(6) A. M. Bond, G. A. Heath, and R. L. Martin, *J. Electrochem. Soc.*, **117**, 1362 (1970).

(7) A. M. Bond, G. A. Heath, and R. L. Martin, *Inorg. Chem.*, **10**, 2026 (1971).

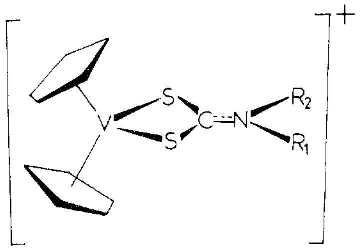


Figure 1. The proposed structure of the $[(cp)_2V(dAdtc)]^+$ cation.

the possibility of an interesting $\overrightarrow{E}C\overleftarrow{E}$ type mechanism arises. The term "$\overrightarrow{E}C\overleftarrow{E}$" has been introduced recently by Feldberg and Jeftic[8] to describe systems in which the reduction of a complex ($\overrightarrow{E}$) is followed by a coupled chemical reaction (C) which results in the occurrence of an oxidation step ($\overleftarrow{E}$). Thus the compounds were of interest not only from the chemical viewpoint but also because of the fact that they provide examples of interesting electrochemical mechanisms, as will be shown.

Nomenclature. The following abbreviations have been used in the text: cp, π-bonded cyclopentadiene; dAdtc, dialkyldithiocarbamate(s); Mdtc, monomethyldithiocarbamate; dMdtc, dimethyldithiocarbamate; dEdtc, diethyldithiocarbamate; dPdtc, diisopropyldithiocarbamate; dBdtc, dibutyldithiocarbamate; Ph, phenyl; Et, ethyl; Bu, butyl.

Experimental Section

Polarography. Conventional dc polarograms were recorded in acetone with a Metrohm Polarecord (E261) using 0.1 *M* tetraethylammonium perchlorate as supporting electrolyte. A three-electrode *iR* compensated system using a Metrohm *iR* compensator (E446) was employed for all conventional dc measurements. The reference electrode was a Metrohm Ag-AgCl EA425 electrode (0.1 *M* LiCl) in acetone. The auxiliary (or third) electrode was either a tungsten or a platinum wire, or an Ag-AgCl electrode identical with the reference. Short controlled drop time polarograms were recorded with a Princeton Applied Research Corp. (PAR) electrochemical system, Model 170. A Metrohm Polarographie stand (E354) was utilized to obtain controlled drop times between 0.16 and 0.32 sec.

Most ac polarograms were recorded on the PAR electrochemical system, Model 170; phase-sensitive read-out was used. An applied alternating potential of 10 mV (peak to peak) was employed at frequencies stated in the text. Some total current ac polarograms (10 mV rms, 50 Hz) were recorded using a modified Metrohm system combining the ac modulator (E393), *iR* compensator (E446), and Polarecord (E261). A three-electrode system was used in all ac work. Cyclic and linear sweep voltammograms were recorded with the PAR electrochemical system at both a Metrohm hanging drop mercury electrode (BM-503) and a platinum wire.

All test solutions were thoroughly degassed with acetone-saturated argon (unless otherwise stated) and a continuous stream of argon was passed over the solutions while measurements were being taken. Solutions were thermostated to 20.0 ± 0.1° in a water-jacketed cell.

Preparations. (a) Bis(π-cyclopentadienyl)-*N,N*-dialkyldithiocarbamatovanadium(IV) Tetraphenylborates (or Tetrafluoroborates). The complexes were prepared from $(cp)_2VCl_2$ and the dialkyldithiocarbamates by methods described elsewhere.[1]

(b) Sodium *N,N*-Dialkyldithiocarbamates. The compounds were prepared from CS_2, the appropriate dialkylamine, and NaOH essentially by the method of Klopping and Van der Kerk.[9]

(c) Tetraethylammonium Perchlorate. A 25% solution of Et_4NOH was neutralized with 20% $HClO_4$. The resulting white precipitate was recrystallized twice from EtOH (95%) and finally from MeOH (AR). The final product was dried and stored under vacuum over silica gel.

(d) Bis(*N,N*-diethyldithiocarbamato)mercury(II). The stoichiometric amount of Na(dEdtc) was mixed with mercury(II) nitrate (AR) in water. The resultant cream-colored precipitate was well washed with water and EtOH and dried under vacuum.

(e) Tetraethylammonium Tetraphenylborate. Stoichiometric amounts of Et_4NCl and $NaPh_4B$ were mixed together in water. The resulting white precipitate was well washed with water and dried over silica gel under vacuum.

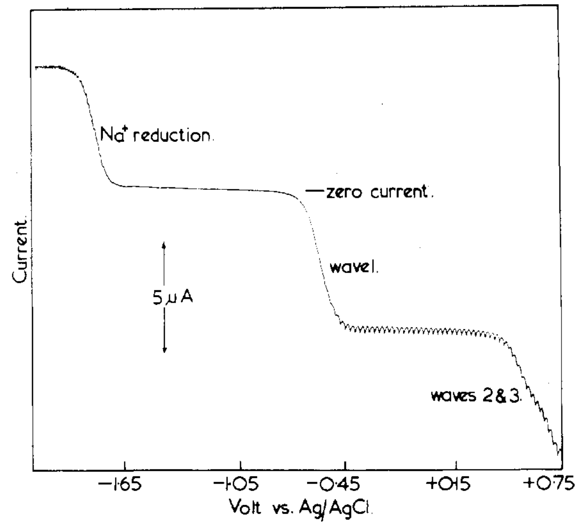


Figure 2. The dc polarogram of Na(dEdtc) (10^{-3} *M*).

Materials. May and Baker "Pronalys" acetone was used for all polarographic and voltammetric measurements. Other chemicals were commercial products.

Results and Discussion

Polarographic Behavior of Sodium *N,N*-Dialkyldithiocarbamates. To aid in the interpretation of the polarographic behavior of the complexes, a complementary study was undertaken on the ligands. Certain dialkyldithiocarbamates have been studied in other media;[10,11] qualitatively similar results have been obtained in acetone. The polarogram illustrated in Figure 2 is typical of each of the compounds examined. The wave at −1.7 V, absent for $[(C_2H_5)_4N]$dEdtc, is the reduction wave for the sodium ion. The other three oxidation waves are characteristic of the dAdtc anion. Two of these occurred close to each other and to the anodic potential limit and hence were difficult to characterize. However, most of the interest in relation to the complexes lay in the wave near −0.5 V (wave 1), which we consider in detail.

Table I lists the half-wave potentials for the various anions at a concentration of 10^{-3} *M* in acetone, while Table II summarizes observations for two anions in the concentration range 10^{-2} to 10^{-4} *M*. For concentrations above 10^{-3} *M*, wave 1 begins to broaden, probably because a new wave appears near −0.4 V. Thus no values of $E_{1/2}$ are recorded above 10^{-3} *M*. At concentrations between 10^{-3} and 10^{-4} *M* the wave height is proportional to $\sqrt{h}$, whereas at concentrations above 10^{-3} *M* the total height of the complex wave (or two waves) follows the same proportionality. Plots of the limiting current *vs.* h are linear at lower concentrations but do not intersect the origin as do the i_d *vs.* $\sqrt{h}$ plots.

The electrocapillary curve of Na(dMdtc) (10^{-3} *M*) is shown in Figure 3. The marked decrease in drop time of the dme in the potential range of wave 1 indicates that the compound and/or product of the anodic reaction is strongly adsorbed. It appears that adsorption is absent at more negative potentials, however, since the two curves are coincident from −1.0 to −2.0 V.

A combination of these results and work in other media[10-12]

---

(8) S. W. Feldberg and L. Jeftic, *J. Phys. Chem.*, **76**, 2439 (1972).

(9) H. L. Klopping and G. J. M. Van der Kerk, *Recl. Trav. Chim. Pays-Bas*, **70**, 936 (1951).

(10) W. Stricks and S. K. Chakravarti, *Anal. Chem.*, **34**, 508 (1962).

(11) D. J. Halls, A. Townshend, and P. Zuman, *Anal. Chim. Acta*, **41**, 51 (1968), and references therein.

(12) D. J. Halls, A. Townshend, and P. Zuman, *Anal. Chim. Acta*, **40**, 459 (1968).

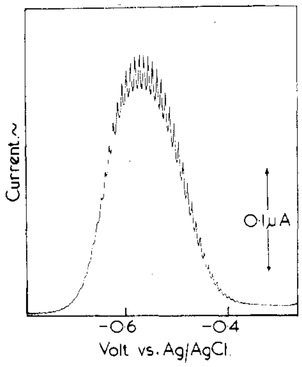


Figure 3. The ac polarogram of wave 1 (Na(dBdtc), 10^{-4} *M*). The frequency was 50 Hz and the alternating potential 10 mV rms.

Table I. Half-Wave Potentials of Na(dAdtc) at 10^{-3} *M* ($E_{1/2}$ in V *vs.* Ag-AgCl)[a]

Na(dAdtc)	Wave 1	Wave 2	Wave 3
Na(dMdtc)	−0.502	+0.60	+0.70
Na(dEdtc)	−0.505	+0.57	+0.72
Na(dPdtc)	−0.550	+0.55	+0.74
Na(dBdtc)	−0.514	+0.53	+0.71
Na(Mdtc)	−0.510	+0.59	+0.70

[a] Because of their nature and position (see text) the $E_{1/2}$ values for waves 2 and 3 are given to two significant figures only.

Table II. Dependence of Half-Wave Potential ($E_{1/2}$) and Wave Height (i_d) on Concentration for Na(dAdtc)[a]

	Na(dEdtc)			Na(dBdtc)		
Concn, *M*	$E_{1/2}$, V	$E_{1/4} - E_{3/4}$, V	i_d, μA	$E_{1/2}$, V	$E_{1/4} - E_{3/4}$, V	i_d, μA
10^{-2}			53.0			55.0
5×10^{-3}			27.4			28.0
10^{-3}	−0.505	0.078	5.35	−0.514	0.076	5.60
5×10^{-4}	−0.498	0.074	2.84	−0.505	0.072	3.06
10^{-4}	−0.496	0.076	0.54	−0.505	0.072	0.60

[a] For concentrations above 10^{-3} *M* i_d refers to the total wave height of the two waves in the region of −0.4 to −0.5 V (see text).

suggests that the more negative wave is adsorption controlled at higher concentrations. The limiting current was proportional to a concentration between 10^{-4} and 10^{-3} *M* as was the total limiting current above 10^{-3} *M*. Thus, although adsorption significantly affects the behavior of this oxidation step, the limiting current of the overall electrode process is diffusion controlled.

The ac polarographic behavior of the ligands confirms the dc results. Above 10^{-3} *M* wave 1 showed the complex behavior expected from a combination of an adsorption-controlled electrode process and a "normal" electrode process. At lower concentrations, the wave (Figure 4) exhibited the characteristics expected for a quasireversible ac electrode process or for a reversible charge-transfer step with coupled chemical or adsorption reactions.

It thus seems likely that the electrode process associated with wave 1 is, in its simplest form

$$\mathrm{dAdtc^- + Hg^0 \rightleftarrows Hg^I(dAdtc) + e^-}$$

$$\mathrm{2Hg^I(dAdtc) \overset{rapid}{\rightleftarrows} Hg^{II}(dAdtc)_2 + Hg^0}$$

As would be expected if the above mechanism is essentially correct, the polarogram of $\mathrm{Hg(dEdtc)_2}$ in acetone was found to be identical with that of the dEdtc anion except that the wave corresponding to wave 1 was now cathodic. When Na(dEdtc) was added to the solution of $\mathrm{Hg(dEdtc)_2}$ and the polarogram rerun, a composite cathodic-anodic wave was obtained as illustrated in Figure 5. This is normally taken as evidence that an electrode process is reversible; however, other data obtained suggest that a reversible or quasireversible assignment with other complications is more appropriate.

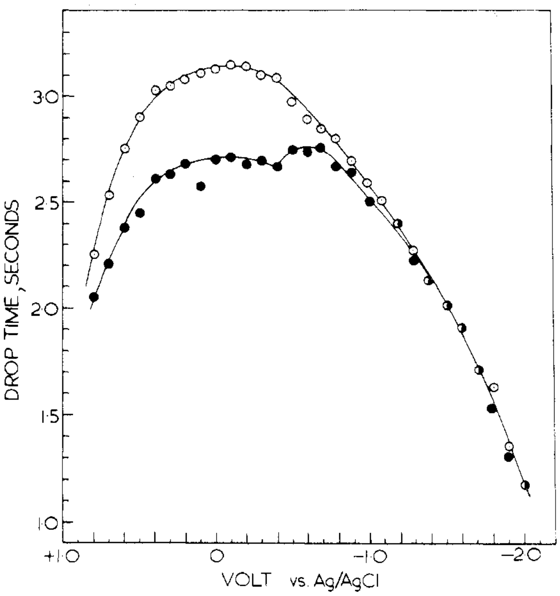


Figure 4. The electrocapillary curves (dme at h = 74 cm) of (a) 0.1 *M* $\mathrm{Et_4NClO_4}$ in acetone (○) and (b) solution (a) plus 10^{-3} *M* Na(dEdtc) (●).

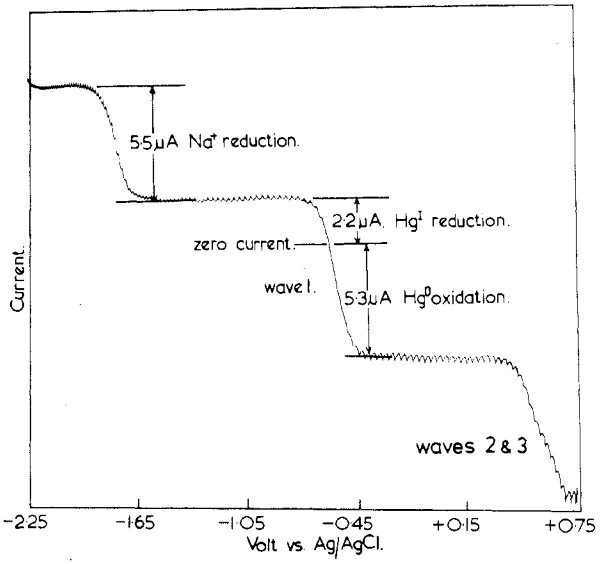


Figure 5. The composite cathodic-anodic dc polarogram of $\mathrm{Hg(dEdtc)_2}$ and Na(dEdtc). The wave height of the $\mathrm{Na^+}$ reduction wave approximates to the anodic current of the composite wave 1, while the cathodic portion of the wave corresponds to that obtained from the $\mathrm{Hg(dEdtc)_2}$ complex prior to the addition of Na(dEdtc).

Plots of log $[(i_d - i)/i]$ *vs.* E and the ac data are consistent with $n = 1$, and not $n = 2$. Furthermore, we have found the wave height of the one-electron sodium ion reduction is approximately equal to that of the mercury oxidation. It is concluded that the anodic wave 1 obtained from the polarogram of solutions containing dAdtc anions arises from the oxidation of mercury rather than the ligand itself. This oxidation is followed by a rapid decomposition step which yields the mercury(II) dialkyldithiocarbamate. The oxidation waves 2 and 3 observed in polarograms of Na(dAdtc) remain anodic in the polarogram of $\mathrm{Hg(dEdtc)_2}$ and occur at approximately the same potentials. They are almost certainly due to oxidations involving the $Hg^{II}(dAdtc)_2$ [or $Hg^{I}(dAdtc)$] compounds.

Results obtained for NaMdtc were similar to those of the dialkyldithiocarbamates except that a further wave was seen on the positive potential side of wave 1. This phenomenon has been observed in other media and has been attributed to a different mercury oxidation process deriving from the removal of a hydrogen ion from the monoalkyldithiocarbamate.[12]

Polarographic Behavior of the Tetraphenyl- and Tetrafluoroborate Anions. The polarogram of Et_4NPh_4B exhibited one oxidation wave at +0.484 V, while that of $NaBF_4$ gave only the wave arising from the reduction of the sodium ion.

Polarographic Behavior of the Complexes. For each of the $[(cp)_2V(dAdtc)][X]$ complexes two one-electron reduction waves were observed (see Table III and Figure 6). Wave 1, the more positive wave, was diffusion controlled in all cases. The diffusion current showed a linear dependence on concentration within the range 10^{-3} to 10^{-4} *M* while the half-wave potentials were independent of concentration. 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 obtained from reversible one-electron reductions. Ac polarograms recorded using conventional or short controlled-rate drop times had half-widths of 90 ± 2 mV over the frequency range 50-600 Hz. The reversibility of this reduction in the ac sense is further evidenced by a comparison of the theoretical wave expected for such a process[13] with that obtained experimentally (see Figure 7) and by the direct proportionality between the ac peak current and the square root of the frequency used. It can therefore be seen that the heterogeneous charge-transfer rate constant for this reduction is very large.

The second (more negative) wave for each compound is drawn out and arises from a nonreversible one-electron reduction. The associated $E_{1/4} - E_{3/4}$ value is large. For each complex the limiting current of this wave is almost identical in magnitude with that obtained from the corresponding reversible wave of the same complex (*i.e.*, wave 1). In the ac sense wave 2 is very broad and, as expected for a nonreversible reduction, has a low peak current relative to the reversible one-electron reduction.

The behavior of the complex $[(cp)_2V(Mdtc)][Ph_4B]$ differed from that of the $[(cp)_2V(dAdtc)][X]$ complexes. Although a reversible wave was observed at −0.418 V, three further waves (a, b, c) were obtained at lower potentials (see Figure 8). Since the only difference between this complex and the $[(cp)_2V(dAdtc)][Ph_4B]$ compounds is the replacement of one alkyl group on the dAdtc ligand by a hydrogen atom, the change in behavior must be attributable to this. Wave a occurs at a potential more negative than that for the reduction of free hydrogen ions (∿1.0 V) and thus may be due to the reduction of the hydrogen atom attached to the ligand. The height of this wave is only marginally lower than that of wave 1, but the heights of waves b and c are substantially less. Wave b has a potential similar to those obtained from wave 2 of the $[(cp)_2V(dAdtc)][Ph_4B]$ complexes, while a polarogram of methylamine showed a wave at exactly the same potential as that at which wave c occurred. It would therefore seem that the processes associated with waves a, b, c involve the partial dissociation of the Mdtc ligand itself, in addition to the usual reduction process occurring for wave 2.

Table III. Half-Wave Potentials ($E_{1/2}$) for the Complexes (V *vs.* Ag-AgCl)

Compd	Wave 1		Wave 2	
	$E_{1/2}$	$E_{1/4} - E_{3/4}$	$E_{1/2}$	$E_{1/4} - E_{3/4}$
$[(cp)_2V(dMdtc)][Ph_4B]$	−0.416	0.059	−1.654	0.120
$[(cp)_2V(dMdtc)][BF_4]$	−0.411	0.060	−1.650	0.105
$[(cp)_2V(dEdtc)][Ph_4B]$	−0.415	0.060	−1.710	0.120
$[(cp)_2V(dEdtc)][BF_4]$	−0.408	0.058	−1.697	0.119
$[(cp)_2V(dPdtc)][Ph_4B]$	−0.428	0.058	1.795	0.108
$[(cp)_2V(dBdtc)][Ph_4B]$	−0.422	0.060	−1.742	0.088
$[(cp)_2V(Mdtc)][Ph_4B]$	−0.418	0.060	*a*	

[a] Three further waves at −1.430 V ($E_{1/4} - E_{3/4} = -0.068$ V), −1.742 V, and −1.867 V, respectively.

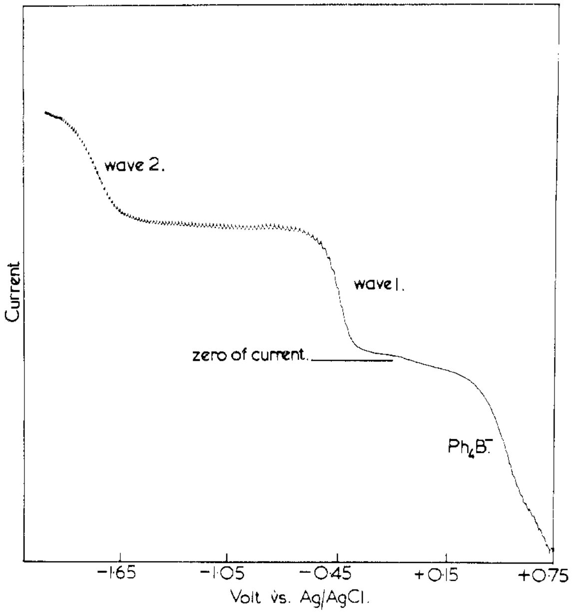


Figure 6. The dc polarograms of $[(cp)_2V(dBdtc)][Ph_4B]$ (5×10^{-4} *M*).

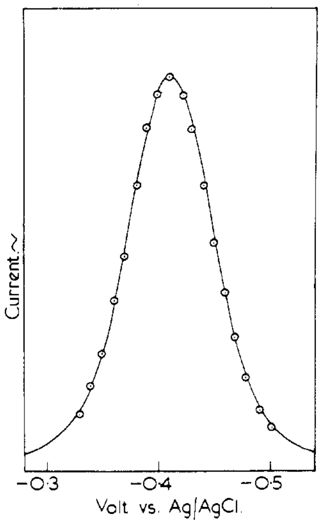


Figure 7. A theoretical-experimental correlation between the shape expected for a reversible one-electron ac wave (solid line) and experimental points taken from the ac wave 1 of $[(cp)_2V(dBdtc)][Ph_4B]$ (circles). The experimental polarogram was recorded at 400 Hz using an alternating potential of 10 mV peak to peak.

The dimethyl and to a lesser extent the diethyl complex showed a deviation in the limiting current region of the reversible dc wave (*i.e.*, at about −0.5 V) as shown in Figure 9. No evidence of such behavior was found with the other complexes. If extreme caution was taken to remove molecular oxygen from the system, no evidence of an ac elec-

---

(13) A. M. Bond, *J. Electroanal. Chem.*, 35, 343 (1972).

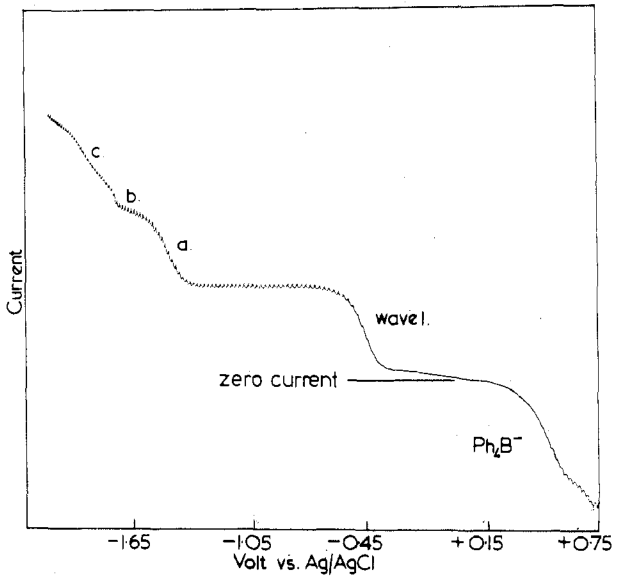


Figure 8. The dc polarogram of $[(cp)_2V(Mdtc)][Ph_4B]$ (5×10^{-4} *M*).

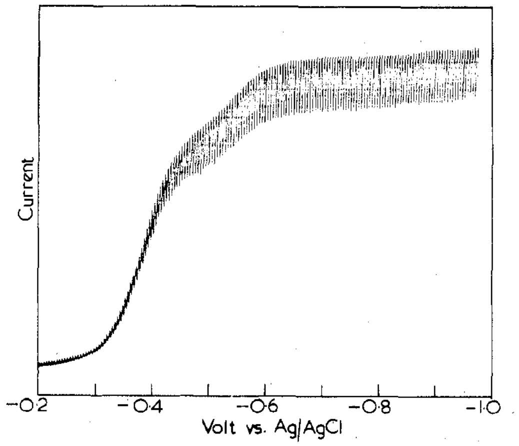


Figure 9. The dc polarogram of wave 1 for $[(cp)_2V(dMdtc)][Ph_4B]$.

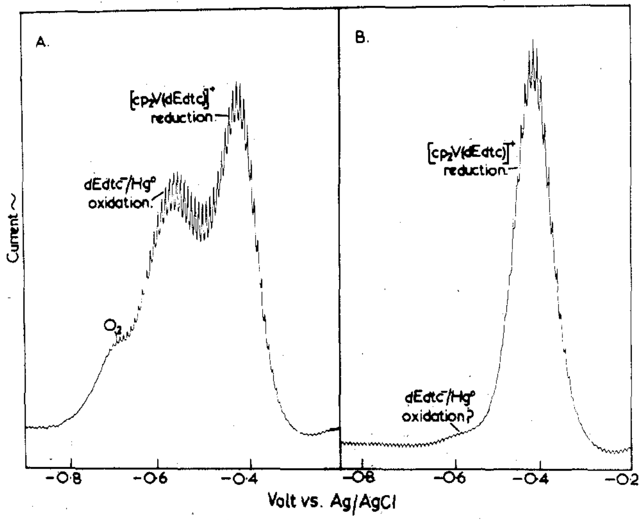


Figure 10. (A) The ac polarogram of $[(cp)_2V(dEdtc)][Ph_4B]$ in the region of wave 1 and in the presence of oxygen. (B) The same polarogram in the absence of oxygen. Both polarograms were recorded at 50 Hz using an alternating potential of 10 mV rms.

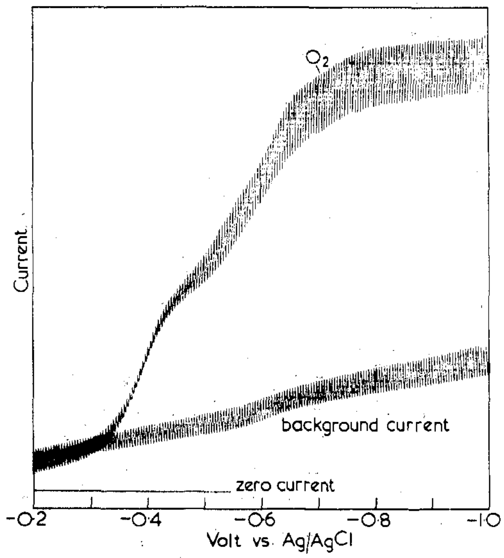


Figure 11. The dc polarogram of $[(cp)_2V(dMdtc)][BF_4]$ in the presence of oxygen.

trode process corresponding to this dc phenomenon was apparent, except for the $[(cp)_2V(dMdtc)][X]$ and $[(cp)_2V(dEdtc)][X]$ complexes (see Figure 10B). However, if oxygen was allowed to enter the system slowly, a new ac wave (in addition to that caused by the nonreversible reduction of molecular oxygen at about −0.7 V) was seen to grow at about −0.5 V (see Figure 10A). When the system was repurged of oxygen, the polarogram reverted to that shown in Figure 10B. The same effect was clearly evident on the dc wave. In the absence of oxygen (as can be seen from Figure 9) the limiting current was constant at −0.7 V. However, when oxygen was present, the wave at about −0.5 V was greatly enhanced in the dc polarogram also (see Figure 11). When free dAdtc anion was added to a solution of its corresponding complex, the deviation in the wave at about −0.5 V grew substantially and an anodic current was observed in the dc polarography.

Much more convincing evidence of the nature of the electrode process was obtained from ac measurements where addition of free ligand introduced another wave whose peak potential and shape coincided exactly with the new wave obtained by introducing oxygen into the system. Furthermore, addition of free ligand to a nondeoxygenated solution simply had the effect of increasing the magnitude of the alternating current at −0.5 V. Thus it would appear that the seemingly anomalous polarographic behavior of the complexes is caused by release of the dAdtc anion subsequent to the initial reduction and that the release of the ligand is catalyzed by oxygen. The ac peak height of wave 1 decreased markedly in the presence of oxygen (see Figure 10) since the associated reaction complicates the electrode process.

The lack of an anodic current in the dc polarograms of the complexes at potentials more positive than the first reduction wave proves that free dAdtc anion is not present in solution as impurity (see Figure 11). The situation is therefore quite exceptional, since the released dAdtc anion causes mercury to be oxidized at a more negative potential than that required for the first reduction step of the complexes (see Tables I and III). Indeed, few reports of such a phenomenon occur in the literature[8,14-18] and it is only recently that these types of electrode processes have been considered in any detail.

[14] E. Fischerova, O. Dracka, and M. Meloun, *Collect. Czech. Chem. Commun.*, 33, 473 (1968).

[15] N. Tanaka and K. Ebata, *J. Electroanal. Chem.*, 8, 120 (1964).

[16] H. A. Laitinen and P. Kivalo, *J. Amer. Chem. Soc.*, 75, 2198 (1953).

[17] N. Tanaka and A. Yamada, *Bull. Chem. Soc. Jap.*, 39, 920 (1966).

[18] H. B. Herman and P. M. Sorana, submitted for publication.

The complete mechanism of the electrode processes associated with the first reduction step of the compounds may now be written

$$[(cp)_2V^{IV}(dAdtc)]^+ + e^- \rightleftarrows [(cp)_2V^{III}(dAdtc)]^0 \qquad (\vec{E})$$

$$[(cp)_2V^{III}(dAdtc)]^0 \underset{k_b}{\overset{k_f}{\rightleftarrows}} \text{``}[(cp)_2V^{III}]\text{''} + dAdtc^- \qquad (C_1)$$

$$dAdtc^- + Hg^0 \rightleftarrows Hg^I(dAdtc) + e^- \qquad (\overleftarrow{E})$$

$$2Hg^I(dAdtc) \overset{\text{rapid}}{\rightleftarrows} Hg^{II}(dAdtc)_2 + Hg^0 \qquad (C_2)$$

where k_f and k_b are the forward and reverse rate constants. Thus the system provides an example of an unusual $\vec{E}C\overleftarrow{E}$ mechanism and, because of the processes associated with the release of dAdtc anions, has been termed here an $\vec{E}C_1\overleftarrow{E}C_2$ mechanism.

It has been suggested that highly reversible reductions observed in other complexes between transition metals and dithio chelates owe their reversibility to their associated π-electron systems;[4] *i.e.*, it is thought that an electron is able to flip quite freely into and from molecular orbitals of the π-electron system inherent to the metal–dithiochelate ring. Although a π system exists for the complexes of this paper, it is more likely that the electron associated with the $\vec{E}$ step above is accommodated in a nonbonding orbital of the vanadium atom directed between the two sulfur atoms of the dithio chelate. Since epr measurements[3] have indicated that this orbital makes little or no contribution to the π system, the electron uptake is associated with the metal only. It is pertinent to note that a highly reversible one-electron reduction step was also observed from corresponding complexes of the type $[(cp)_2V(L)][BF_4]$, where L is a chelating agent coordinating to vanadium through two oxygen atoms and therefore where there is no extensive delocalized metal–chelate π-electron system.[19]

The dissociation of the neutral vanadium(III) complex obtained from the initial reduction is apparently only very slight in the absence of oxygen but is greatly enhanced by its presence in even minute traces. A significant amount of dissociation was still evident in dc polarograms in which there was no trace of waves due to the reduction of oxygen. The oxygen catalysis of step C_1 is readily explicable in terms of the chemistry of vanadium. Vanadium has been termed a class "a" metal under the classification of Ahrland, Chatt, and Davies,[20] and thus at first the stability of these complexes to oxygen and water seems surprising. Apparently the presence of the cyclopentadienyl groups bestows upon the vanadium(IV) atom properties more characteristic of later 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 $[(cp)_2Ti^{III}(dAdtc)]^0$ complexes are highly oxygen sensitive[21]), and the resulting formation of oxovanadium species could quite easily cause the release of the dAdtc anion. Since the addition of water to test solutions caused no discernible change in polarographic behavior, the decomposition of the $[(cp)_2V^{III}(dAdtc)]^0$ species in the absence of polarographically detectable oxygen must result from minute traces of oxygen or simply from the lowered stability of this neutral species relative to the cationic vanadium(IV) species. Step C_1 was more pronounced in dc polarograms of the $[(cp)_2V(dMdtc)][X]$ and $[(cp)_2V(dEdtc)][X]$ complexes than in those of the $[(cp)_2V(dPdtc)][Ph_4B]$ and $[(cp)_2V(dBdtc)][Ph_4B]$ compounds. Also evidence of a wave at ∼−0.5 V was detectable in the ac polarograms of the former two complexes. This may be a reflection of the relative inductive effects of the different alkyl groups.

It is interesting to note that the half-wave potentials varied little with change in the coordinated dAdtc ligand. Substituent effects have been shown markedly to alter the half-wave potentials of some dithioketone transition metal complexes,[4] but since the electron here enters an orbital divorced from the bonding orbitals, the half-wave potentials are expected to be insensitive to such changes. The second reduction step of the complexes, if associated with the metal, would produce a vanadium(II) species. The instability of whatever product does result from this step is emphasized by the nonreversibility of its associated wave, which indicates that significant structural changes follow as a consequence.

Controlled-Potential Electrolysis. Despite many attempts at controlled-potential electrolysis at platinum sheet, tungsten wire, and mercury pool electrodes, no evidence could be found for the formation of the vanadium(III) species. The failure is believed to be due to the dissociation step C_1 which follows the initial reduction and to adsorption, since the current achieved at the commencement of every electrolysis decayed rapidly but could be restored by cleaning or replacing the various electrodes.

Cyclic Voltammetry. The applicability of this technique to the study of ECE-type mechanisms has been well illustrated by Feldberg and Jeftic.[8] These workers have taken into account the modifying effect of a redox cross reaction and have calculated the behavior expected from $\vec{E}C\vec{E}$ and $\vec{E}C\overleftarrow{E}$ mechanisms for a range of dissociation constants of reaction C_1, where the two electron-transfer steps are separated by 0.3 V. The corresponding possible redox cross reaction for this system

$$[(cp)_2V^{IV}(dAdtc)]^+ + dAdtc^- + Hg^0 \rightleftarrows Hg^I(dAdtc) + [(cp)_2V^{III}(dAdtc)]^0$$

is obviously much more complicated than that considered theoretically since step $\overleftarrow{E}$ is followed by a further reaction (C_2) and since oxygen can play an important catalytic role in step C_1. Furthermore, step $\overleftarrow{E}$ is not considered to be completely reversible here as is required in the theoretical treatment. The possible consequences of these complications where therefore borne in mind when comparing our results with those predicted in ref 8.

Samples of cyclic voltammograms obtained at a hanging drop mercury electrode are shown in Figure 12. The slight dissociation (reaction C_1) of the $[(cp)_2V^{III}(dMdtc)]^0$ complex in the absence of oxygen (Figure 12A, B) and the lack of it for the $[(cp)_2V^{III}(dBdtc)]^0$ complex even in the presence of a small amount of oxygen (Figure 12C) are consistent with previous observations. When sufficient oxygen was allowed to enter the system, step C_1 was catalyzed dramatically for all complexes as evidenced by the marked increase of step $\overleftarrow{E}$ (Figure 12D). The addition of free dMdtc anion to a solution of the corresponding complex caused the wave due to ($\overleftarrow{E}$) arising from complex dissociation to grow substantially and the current to become anodic at potentials more positive than that of the $\vec{E}$ step; indeed, for runs on pure complexes the current was slightly anodic in this region subsequent to the initial cycle (Figure 12A, C).

In the theoretical voltammograms of ref 8, the relative values of the respective E° potentials (E° is equivalent to polaro-

---

[19] A. T. Casey, A. M. Bond, and J. R. Thackeray, unpublished results. L = anion of 8-hydroxyquinoline, salicylaldehyde, or acetophenone.

[20] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev., Chem. Soc.*, 12, 265 (1958).

[21] R. S. P. Coutts, P. C. Wailes, and J. V. Kingston, *Aust. J. Chem.*, 23, 463 (1970).

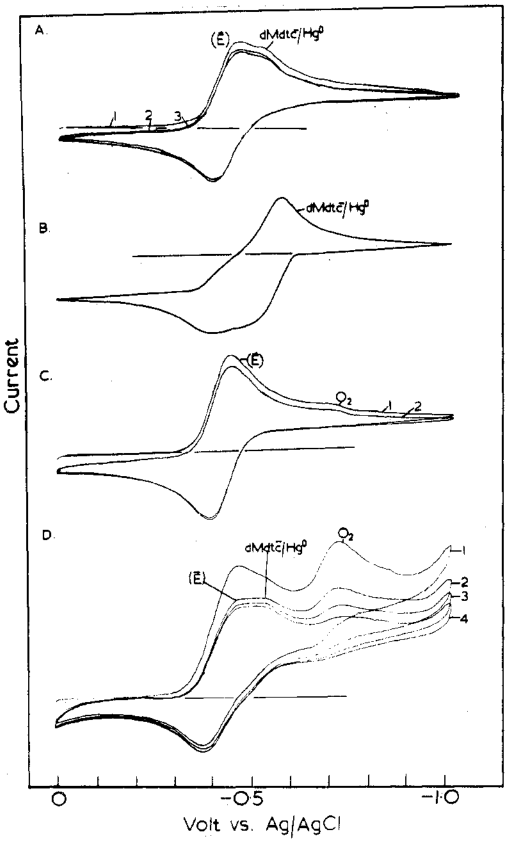


Figure 12. Cyclic voltammograms at a hanging drop mercury electrode (scan rate 100 mV/sec). Successive sweeps are numbered and zero current is marked in each case: A, $[(cp)_2V(dMdtc)][Ph_4B]$ in the absence of oxygen; B, NadMdtc; C, $[(cp)_2V(dBdtc)][Ph_4B]$; D, $[(cp)_2V(dMdtc)][Ph_4B]$ in the presence of oxygen.

graphic half-wave potential) for reactions $\vec{E}$ ($E°_1$) and $\overleftarrow{E}$ or $\vec{E}$ ($E°_3$) were indicative of this type of ECE mechanism. For the $\vec{E}C\overleftarrow{E}$ case, and with increasing magnitude of the rate constant for reaction C, the wave from ($\overleftarrow{E}$) grew and for any one voltammogram successive sweeps showed a decrease in the wave height pertaining to ($\vec{E}$) and an increase in that pertaining to ($\overleftarrow{E}$). For cases where both the redox cross reaction and reaction C were exerting a strong influence, the cathodic current dropped substantially (and even became anodic in the extreme case) in the potential region between $E°_1$ and $E°_3$ during the first cathodic sweep.

The behavior of voltammograms obtained here is qualitatively similar to the above theoretical predictions for an $\vec{E}C\overleftarrow{E}$ mechanism, although for reasons mentioned earlier no quantitative comparison can be made. Also, because the potential difference $[E°_1 - E°_3]$ is not as large as that considered theoretically, the effect of increasing the rate constant of (C_1) or of possible cross reactions is not as pronounced as might otherwise be the case. The results are therefore consistent with those expected of an $\vec{E}C\overleftarrow{E}$ mechanism and also with the results obtained from polarography.

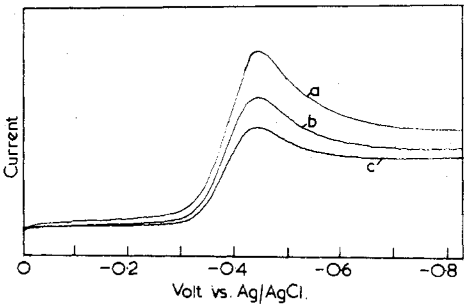


Figure 13. Voltammograms of $[(cp)_2V(dBdtc)][Ph_4B]$ at a platinum electrode recorded using scan rates of (a) 200, (b) 100, and (c) 50 mV/sec (peak potential −0.450 V in all cases).

Linear Sweep and Cyclic Voltammetry at a Platinum Electrode. In the course of electrolysis measurements it was found that voltammograms of the complexes could be recorded successfully at a platinum electrode. The first reduction step remained reversible at this electrode, as shown by the constancy of peak potential over a range of scan rates and by the direct proportionality between the peak height and the square root of scan rate (typical scans are shown in Figure 13). The half-wave potential for reversible one-electron processes is 0.028 V more anodic than the peak potential at 25°.[22] This gives a half-wave potential of −0.422 V for $[(cp)_2V(dBdtc)][Ph_4B]$ at a platinum electrode (*cf.* −0.422 V obtained at the dme).

Cyclic voltammograms at a platinum electrode produced results consistent with those obtained from other techniques. In the absence of oxygen a wave characteristic of reaction ($\vec{E}$) was seen. In the presence of oxygen the cathodic wave from ($\vec{E}$) gradually diminished with successive scans and on anodic sweeps little evidence for a wave was seen since the vanadium(III) species generated by reaction $\vec{E}$ was removed by step C_1. The fact that no wave corresponding to the oxidation step $\overleftarrow{E}$ was obtained in the absence of mercury further verifies the proposed mechanism.

Registry No. Et_4NClO_4, 2567-83-1; Et_4NOH, 77-98-5; $HClO_4$, 7601-90-3; $Hg(dEdtc)_2$, 14239-51-1; Et_4NCl, 56-34-8; $NaPh_4B$, 143-66-8; Na(dMdtc), 128-04-1; Na(dEdtc), 148-18-5; Na(dPdtc), 4092-82-4; Na(dBdtc), 136-30-1; Na-(Mdtc), 137-42-8; $[cp_2V(dMdtc)][Ph_4B]$, 37215-21-7; $[cp_2V(dMdtc)][BF_4]$, 37215-20-6; $[cp_2V(dEdtc)][Ph_4B]$, 37215-23-9; $[cp_2V(dEdtc)][BF_4]$, 37215-22-8; $[cp_2V(dPdtc)][Ph_4B]$, 37215-24-0; $[cp_2V(dBdtc)][Ph_4B]$, 37215-25-1; $[cp_2V(Mdtc)][Ph_4B]$, 37215-19-3; mercury(II) nitrate, 10045-94-0; tetraethylammonium tetraphenylborate, 12099-10-4.

Acknowledgment. J. R. T. thanks the Commonwealth of Australia for a Commonwealth Postgraduate Research Award.

[22] P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience, New York, N. Y., 1954, p 115.