Comparative Electrochemical Studies on a Variety of Bis(π-cyclopentadienyl)vanadium(IV) Chelates in Acetone
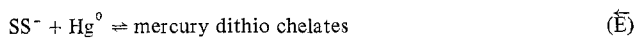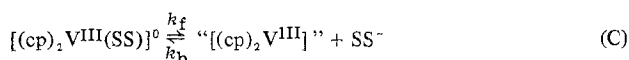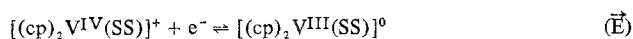
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Electrochemical investigations have been undertaken on complexes formed between the $(\pi\text{-}C_5H_5)_2V^{IV}$ group and a wide variety of chelating ligands. Ac and dc polarography and cyclic and linear sweep voltammetry at both mercury and platinum electrodes have shown that all complexes initially undergo a reversible one-electron reduction to produce $(\pi\text{-}C_5H_5)_2$-V^{III} species. In some of the complexes with chelates coordinating through sulfur donor atoms a follow-up dissociation step is observed which is invariably markedly catalyzed by oxygen. An ECE mechanism results in such circumstances. Vanadium(III) complexes with dioxo chelates do not exhibit any dissociation in the absence of oxygen, on the time scale of the electrochemical experiment. Half-wave potentials for the reversible charge-transfer step are compared for all the complexes studied. The reaction of the vanadium(IV) chelates with Na-Hg amalgam is described along with the identification of two resulting $[(\pi\text{-}C_5H_5)_2V^{III}L]^0$ complexes. All complexes exhibit additional polarographic reduction waves, which are nonreversible.

Introduction

A number of complexes formed between the bis(π-cyclopentadienyl)vanadium(IV) group ($(cp)_2V^{IV}$) and a variety of dithio chelates (SS), dioxo chelates (OO), and other ligands have recently been prepared and characterized in this laboratory.[1-3] Polarographic studies on complexes of the formulation $[(cp)_2V^{IV}(SS)][X]$ (where SS = dialkyldithiocarbamate,[4] O-alkyl xanthate or dialkyl dithiophosphate,[5] and X is a large anion) have shown that they undergo a reversible one-electron reduction to yield the neutral $[(cp)_2V^{III}(SS)]^0$ species. All vanadium(III) complexes thus formed dissociate in the presence of minute traces of oxygen (and even in its absence in many cases) to release the free ligand (SS). This process is readily monitored polarographically since mercury at the dme is oxidized in the presence of these free dithio chelates to give waves at potentials more negative than the initial reduction step of vanadium(IV). Where dissociation is occurring, the overall process has been described by the terminology ECE, *i.e.*

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

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

$$SS^- + Hg^0 \rightleftharpoons \text{mercury dithio chelates} \qquad (\overleftarrow{E})$$

(where k_f and k_b are the forward and backward rate constants). Step E is derived from the oxidation of mercury(0) in the presence of free SS^-, the exact nature of the oxidation depending upon the particular dithio chelate under consideration.[4,5] Extension of these mechanistic studies to ligand groups other than 1,1-dithio chelates has yet to be undertaken.

It has been established in other works[4-9] that systematic electrochemical studies on a wide array of inorganic complexes can provide valuable information concerning their chemical behavior and can serve as a probe into the possibility of synthesizing new compounds. Furthermore, comparative studies between different dithiochelate and other suitable complexes might be expected to yield interesting data concerning electronic and other properties of the metal–ligand system. Comparisons of this type are usually rendered difficult, however, because changing the ligand often alters the stereochemistry of the metal markedly. Such complications are not expected for complexes derived from the $(cp)_2V^{IV}$ group, since they are all likely to be similar in structure—being based on a pseudotetrahedral environment about the central vanadium atom[1] (see Figure 1). Moreover, the electronic configuration of vanadium(IV) is d^1, and thus the electron pertaining to the first reduction step may readily be accommodated in a nonbonding orbital primarily associated with the vanadium atom.[10,11] Half-wave potentials for this reduction wave should therefore reflect the nature of the metal–chelate bonding and the electronic structure of the coordinated chelates.

In this paper the polarographic behavior of a number of complexes not previously reported is described, a comparison is made of half-wave potentials for the first reduction step from all the complexes prepared, and results of further electrochemical and chemical studies on the system are given.

Experimental Section

(a) Preparation of Bis(π-cyclopentadienyl)vanadium(IV) Chelates. The preparation of these complexes has been[1-3] described elsewhere.

(b) Instrumentation and Experimental Details. Instrumentation and experimental conditions are those described previously.[4,12] Acetone was used as the solvent in all instances. Potentials are reported as volts *vs.* Ag–AgCl (0.1 *M* LiCl; acetone). Tetraethylammonium perchlorate (0.1 *M*) was used as the supporting electrolyte and solutions were thermostated at 20 ± 0.1°.

Nomenclature

Structures of the various ligand anions which have been chelated to the $(cp)_2V^{IV}$ group are shown in I–XV. The following abbreviations have been used: (I) *N,N*-dialkyldithiocarbamate, dadtc; (II) *O*-

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

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

(3) J. R. Thackeray, Ph.D. Thesis, University of Melbourne, 1973.

(4) A. M. Bond, A. T. Casey, and J. R. Thackeray, *Inorg. Chem.*, **12**, 887 (1973).

(5) A. M. Bond, A. T. Casey, and J. R. Thackeray, submitted for publication in *J. Chem. Soc., Dalton Trans.*

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

(7) D. C. Olson, V. P. Mayweg, and G. N. Shrauzer, *J. Amer. Chem. Soc.*, **88**, 4876 (1966).

(8) G. S. Patterson and R. H. Holm, *Inorg. Chem.*, **11**, 2285 (1972).

(9) J. G. M. Van der Linden, *J. Inorg. Nucl. Chem.*, **34**, 1645 (1972).

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

(11) W. E. Douglas and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1796 (1972).

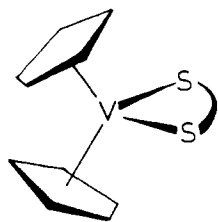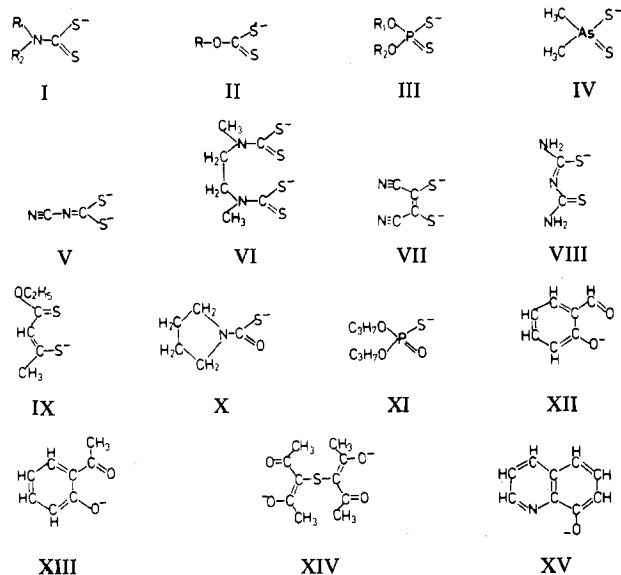(12) A. M. Bond and J. R. Thackeray, *Chem. Instrum.*, **4**, 299 (1972).

Figure 1. Predicted structure type for bis(π-cyclopentadienyl)vanadium(IV) chelates.

alkyl xanthate, axan; (III) O,O'-dialkyl dithiophosphate, dadtp; (IV) dimethyl dithioarsinate (or dithiocacodylate), dtcac; (V) N-cyanodithiocarbimate, cdtc; (VI) N,N'-dimethylethylenebis(dithiocarbamate), dmebdtc; (VII) maleonitriledithiolene, mnt; (VIII) dithiobiuret, dtb; (IX) O-ethyl thioacetothioacetate, OEtSacSac; (X) N-pyrrolidine-monothiocarbamate, pmtc; (XI) O,O'-diisopropyl monothiophosphate, dpmtp; (XII) salicylaldehyde, sal; (XIII) o-acetylphenol, ap; (XIV) 3,3'-thiobis(pentane-2,4-dione), S$_1$(acac)$_2$; (XV) 8-quinolinol, oxine. Abbreviations used for the alkyl (R) groups of dithiocarbamate, xanthate, and dithiophosphate derivatives are as follows: methyl, m; ethyl, e; propyl, p; butyl, b; octyl, o; 2-chloroethyl, e$_{Cl}$. Whence, *e.g.*, diethyldithiocarbamate is abbreviated to dedtc. In the general context Et has been used for ethyl.

Results

Results for all the complexes are listed in Table I, along with relevant comments where necessary. Data were obtained using dc and ac polarography and cyclic voltammetry.

The complexes can be classified according to the ligand grouping. Ligands I–V are 1,1-dithiolates. Maleonitriledithiolate (VII) is a 1,2-dithiolate, while ligands VIII and IX are 1,3-dithiolates. Comparison of ligands I–IX provides variation in ring size. Ligands X and XI are 1,1-monothiolates in which one sulfur ligand is replaced by an oxygen group. The remainder of the ligands, except for XV, provide examples of dioxo ligands where both sulfur groups are replaced by oxygen. Finally, 8-quinolinol (XV) and (cp)$_2$VCl$_2$ are included to complete the study.

Many of the sulfur ligands gave dissociative ECE mechanisms. Ligand dissociation was almost invariably catalyzed markedly by the presence of oxygen. Figure 2 shows the catalytic influence of oxygen with the dithiocacodylate complex. The nature of the mercury oxidation in the presence of this and other 1,1-dithio ligands has been described elsewhere.[13] On replacement of one sulfur by oxygen, the same
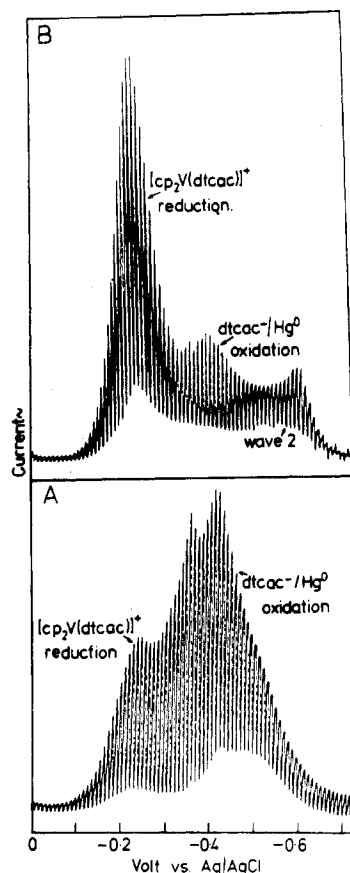
(13) A. M. Bond, A. T. Casey, and J. R. Thackeray, *J. Electrochem. Soc.*, 120, 1502 (1973).

Figure 2. Ac polarographic behavior of [(cp)$_2$V(dtcac)][BF$_4$] in the presence (A) and absence (B) of oxygen.

effect is observed (Figure 3). However, when both sulfurs were replaced, the presence of oxygen has little or no influence (Figure 4).

The compound (cp)$_2$VCl$_2$ has been studied previously by Dessy, *et al.*,[14] who also observed two reduction waves (Figure 5). The following mechanism was postulated

$$(cp)_2V^{IV}Cl_2 \xrightarrow{e^-} (cp)_2V^{III}Cl \xrightarrow{e^-} \underset{(\text{vanadocene})}{(cp)_2V^{II}} + Cl^-$$
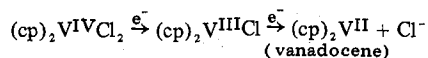
Our observation that neither process is completely reversible is consistent with the above mechanism. However, if (cp)$_2$-VCl$_2$ remains undissociated in acetone, then by analogy with other complexes the electron transfer conceivably could be reversible, and the slow step may be dissociation of chloride, *i.e.*

$$(cp)_2V^{IV}Cl_2 \underset{\rightleftarrows}{\overset{e^-}{}} (cp)_2V^{III}Cl_2 \xrightarrow{kf} (cp)_2V^{III}Cl + Cl^-$$
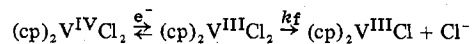
Discussion

It is our belief that the electron of the first reduction step is accommodated in an orbital associated largely with the metal and therefore that vanadium(III) species result. Molecular orbital schemes proposed for (cp)$_2$MX$_2$ type systems predict that three "nonbonding" metal orbitals remain after metal–cyclopentadienyl bonds have been accounted for.[10,11] Two of these may be engaged for further bonding, while the third orbital remains nonbonding and contains any electrons over and above the 12 involved in the metal–cyclopentadienyl bonds. For the case at hand (d^1), there is therefore a site available in the nonbonding orbital for a further electron.

(14) R. E. Dessy, R. B. King, and M. Waldrop, *J. Amer. Chem. Soc.*, 88, 5112 (1966).

Table I. Polarographic Data for Reduction of Bis(π-cyclopentadienyl)vanadium(IV) Chelates

Complex	Wave 1				Further waves (nonreversible), $E_{1/2}$, V vs. Ag–AgCl	Comments
	$E_{1/2}$, V vs. Ag–AgCl	$E_{1/4} - E_{3/4}$, V	$E_{1/2}(\text{Hg}^0$ oxidn),^{f} V	Ac half-width (wave 1), mV		
[(cp)₂V(dpmtp)][Ph₄B]	+0.010	0.066		105 (20 Hz), 152 (300 Hz)	−1.5	a (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[(cp)₂V(de$_\text{Cl}$dtp)][Ph₄B]	−0.060	0.067			−0.64	a, b (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[(cp)₂V(dmdtp)][BF₄]	−0.082	0.064			−0.63	a, b (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[(cp)₂V(dodtp)][Ph₄B]	−0.104	0.068			−0.66	a, b (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[(cp)₂V(dbdtp)][Ph₄B]	−0.122	0.068			−0.63	a, b (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[(cp)₂V(dpdtp)][Ph₄B]	−0.124	0.066			−0.67	a, b (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[(cp)₂V(dedtp)][Ph₄B]	−0.132	0.066	−0.142^g		−0.70	a, b (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
(cp)₂VCl₂	−0.195	0.090			−1.43	
[(cp)₂V(dtcac)][BF₄]	−0.215	0.072	−0.378^g		−0.55	a (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[(cp)₂V(mxan)][BF₄]	−0.243	0.060			−1.39, −1.9	a, b (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[(cp)₂V(exan)][BF₄]	−0.254	0.060	−0.365^g		−1.38, −1.8	b, c (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[(cp)₂V(pxan)][BF₄]	−0.274	0.060			−1.45, −1.9	b, c (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[(cp)₂V(bxan)][BF₄]	−0.288	0.062			−1.44, −1.9	b, c (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[(cp)₂V(chxan)][BF₄]	−0.300	0.060			−1.44, −1.9	b, c (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[(cp)₂V(dtb)][PF₆]	−0.365	0.056		100 (300 Hz)	−1.4, −1.5	c
[(cp)₂V(sal)][BF₄]	−0.365	0.060		88 (300 Hz)	−1.22, −1.48	c
[(cp)₂V(OEtSacSac)][BF₄]	−0.392	0.055			−0.65	c
[(cp)₂V(mdtc)][Ph₄B]	−0.418	0.060			−1.43, −1.74, −1.87	a, d (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[(cp)₂V(dmdtc)][Ph₄B]	−0.416	0.059			−1.65	a, d (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[(cp)₂V(dedtc)][Ph₄B]	−0.415	0.060	−0.505^h		−1.71	a, d (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[(cp)₂V(dpdtc)][Ph₄B]	−0.428	0.058			−1.80	c, d (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[(cp)₂V(dbdtc)][Ph₄B]	−0.422	0.060			−1.74	c, d (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[((cp)₂V)₂(μ-dmebdtc)][PF₆]₂	−0.420	0.090		135 (300 Hz)	−1.30	a (E$\vec{\text{C}}\overleftarrow{\text{E}}$)
[(cp)₂V(ap)][BF₄]	−0.420	0.056		88 (300 Hz)	−1.30, −1.53	c (ECE)
[(cp)₂V(pmtc)][BF₄]	−0.430	0.060		89 (300 Hz)	−1.45	c
[((cp)₂V)₂(μ-S₁(acac)₂)][BF₄]₂	−0.437	0.062		95 (300 Hz)	−1.0, −1.8	
[(cp)₂V(oxine)][BF₄]	−0.465	0.060		88 (300 Hz)	−1.39, −1.69, −1.93	e
[(cp)₂V(mnt)]	−0.560	0.056		88 (300 Hz)	−1.57	
[(cp)₂V(cdtc)]	−0.603	0.060		86 (300 Hz)	−1.58	c

^{a} Wave 1 shows ligand dissociation from reduced species even in the absence of oxygen. Ligand dissociation markedly catalyzed by the presence of oxygen. ^{b} See ref 5 for further details. ^{c} No ligand dissociation from reduced species in the absence of oxygen but ligand release markedly catalyzed in its presence. ^{d} See ref 4 for further details. ^{e} No ligand dissociation discernible even in the presence of a significant amount of oxygen. ^{f} See text. ^{g} $E_{1/2}$ for 3SS⁻ + Hg⁰ $\rightleftharpoons$ Hg$^{\text{II}}$(SS)₃ + 2e⁻. ^{h} $E_{1/2}$ for SS⁻ + Hg⁰ $\rightleftharpoons$ Hg$^{\text{I}}$(SS) + e⁻ and 2Hg$^{\text{I}}$(SS) $\rightleftharpoons$ Hg(SS) + Hg.

This orbital is not significantly involved with bonding to any ligands, since in esr spectra the vanadium nuclear hyperfine splitting parameter remained almost constant for all the different chelate complexes studied[1-3]—indicating that the ligand nature had little influence on delocalization of the unpaired electron.

The extreme air sensitivity of reduced species is consistent with the chemistry of vanadium(III), and no polarographic reduction waves were seen down to the solvent limit (*i.e.*, −2.2 V) for the free dithio chelate ligand anions (except for mnt²⁻). Furthermore, all $E_{1/2}$ values for the first reduction step fell within a range of ∼0.6 V (see Table I), despite the variety of different ligands coordinated to the (cp)₂V$^{\text{IV}}$ group. A greater variation might be expected if the electron was entering an orbital of substantial ligand character. The nature of molecular orbitals will of course vary somewhat, depending upon the chelate, and low-lying unoccupied orbitals of ligand character are most likely where the chelate is a 1,2-dithiolene[15] (*e.g.*, mnt). Finally, esr spectra[16] on reduced species indicated vanadium(III), since the strong signal typical of vanadium(IV)[1] disappeared (see later discussion). Thus, available evidence is consistent with the reduc-

tion step involving a metal orbital of considerable metal character.

The first reduction step for many of the complexes was completely reversible (see Table I), and for such cases the associated charge transfer was in fact very rapid, since the corresponding ac waves maintained half-widths near 88 mV even at high frequencies. Deviations from reversible behavior for the complexes with dadtp, dtcac, dmebdtc and a few other ligands are thought to be due to complex dissociation (*i.e.*, step C) rather than irreversible charge-transfer processes. This is readily verified for the dithio chelate complexes mentioned above because extra waves due to released ligand (*i.e.*, steps E) were seen in almost all these cases even in the absence of oxygen. The occurrence of E$\vec{\text{C}}\overleftarrow{\text{E}}$ mechanisms proved very fortunate since step $\overleftarrow{\text{E}}$ provided visible evidence of complex dissociation and enabled the electrode processes to be interpreted.

Before discussing trends in dc half-wave potentials (or ac peak potentials (E_p)), it is necessary to establish the relationship between $E_{1/2}$ (or E_p) values and the E° parameter for the corresponding V$^{\text{IV}}$–V$^{\text{III}}$ couple. If the rate constant k_f in the process

$$(\text{cp})_2\text{V}^{\text{III}}\text{L} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \text{``(cp)}_2\text{V}^{\text{III}}\text{''} + \text{L}^-$$
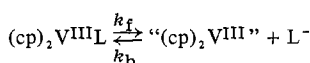
(where L is a chelate) is of comparable magnitude to k_b and if both are fast enough to ensure that equilibrium conditions

(15) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968), and references therein.

(16) We are grateful to Ira Goldberg (North American Rockwell Science Center, Canoga Park, Calif.) for recording esr spectra of reduced species.
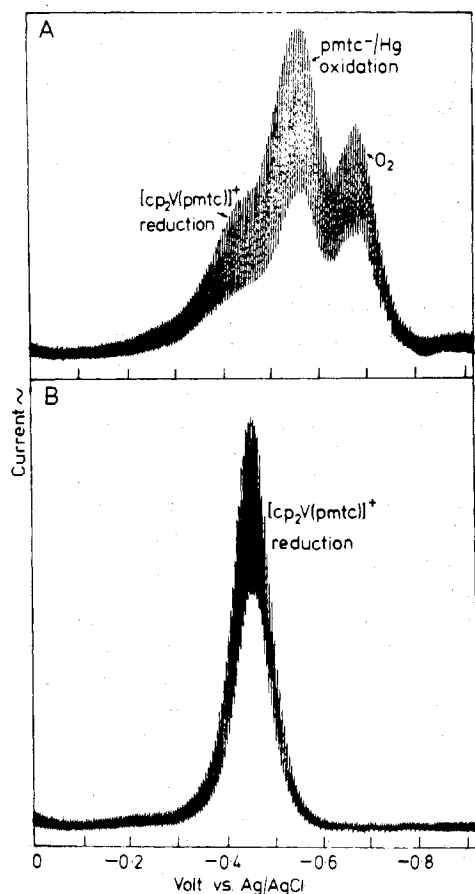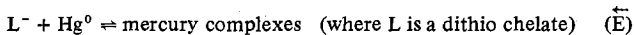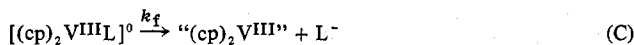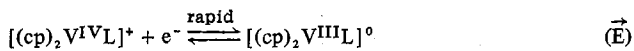
Figure 3. Ac polarographic behavior of [(cp)$_2$V(pmtc)][BF$_4$] in the presence (A) and absence (B) of oxygen.

Figure 4. Ac polarographic behavior of [(cp)$_2$V(oxine)][BF$_4$] in the presence (A) and absence (B) of oxygen.

Figure 5. Dc polarogram of (cp)$_2$VCl$_2$ (controlled drop time).

apply, then the $E_{1/2}$ and E_p values will vary with the concentration of L$^-$ (since the concentration of (cp)$_2$V^{III}L will depend on the concentration of L$^-$). To test the influence of this follow-up chemical reaction on E_p, ac voltammetry was undertaken at a platinum electrode. The dme was discarded to eliminate processes associated with the oxidation of mercury (*i.e.*, $\vec{E}$ steps). In these circumstances the electrode mechanisms under study were reduced to $\vec{E}C$, or simply $\vec{E}$ where k_f is very small (*i.e.*, step C is negligible).

The peak potential of step $\vec{E}$ was measured as a function of ligand concentration (by adding varying amounts of free ligand to test solutions) and found to be completely independent of this factor for all the complexes. Therefore, in cases where dissociation of vanadium(III) species occurs, it appears that step C is not an equilibrium and the overall electrode process can now be written more specifically as

$$[(cp)_2V^{IV}L]^+ + e^- \underset{\text{rapid}}{\overset{}{\rightleftharpoons}} [(cp)_2V^{III}L]^0 \qquad (\vec{E})$$

$$[(cp)_2V^{III}L]^0 \xrightarrow{k_f} \text{``(cp)}_2V^{III}\text{''} + L^- \qquad (C)$$

$$L^- + Hg^0 \rightleftharpoons \text{mercury complexes} \quad \text{(where L is a dithio chelate)} \qquad (\overleftarrow{E})$$

Nevertheless, where dissociation is significant, the concentration of [(cp)$_2$VL]^0 species will be lowered, and the measured half-wave or peak potentials will no longer be exactly equivalent to E° (V^{IV}-V^{III}) because of the kinetic perturbation. (An example of this case is provided by the dithiophosphate series.) If, on the other hand, no dissociation occurs, the half-wave and peak potentials will be equivalent to E°(V^{IV}-V^{III}), provided the reduced and oxidized forms have equal diffusion coefficients. (An example of this case is provided
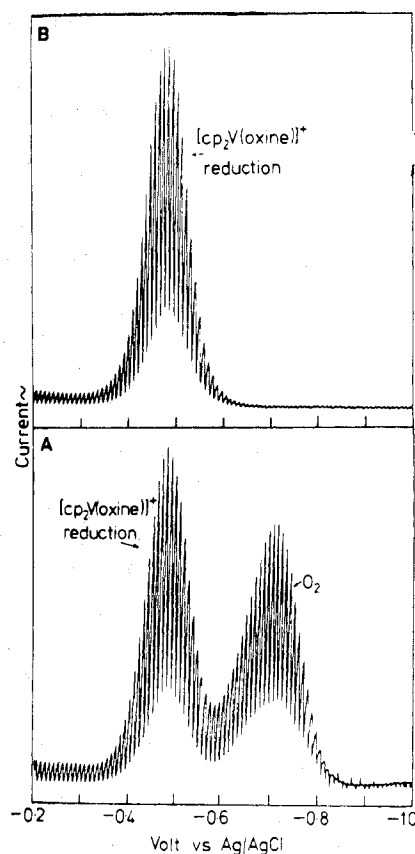
by the xanthate series.) In most instances where dissociation was found, the effect on the reversible $E_{1/2}$ value is considered only slight. We have therefore used measured $E_{1/2}$ values for the purposes of qualitative comparison of the various chelate systems, believing that the slight differences mentioned above are insignificant compared to the changes in $E_{1/2}$ (or E°) values brought about by changing the coordinated chelates.

No thermodynamic significance can be attached to the half-wave potentials for the second and subsequent reduction steps since they were nonreversible in all cases. This may be predicted on the basis of the proposed bonding schemes.

The observation of an $\vec{E}C\vec{E}$ mechanism at the mercury electrode has been made for members of the dithiocarbamate, dithiophosphate, and xanthate series and for complexes with other sulfur-containing ligands. In all these complexes the half-wave potential of step $\vec{E}$ was slightly more positive than

that for the first (most negative) oxidation of mercury(0) in the presence of the free dithiolate anion. However, as the respective half-wave potentials reflect the stabilities of the vanadium(IV) species with respect to the vanadium(III) species and of the mercury(II) dithio chelates with respect to mercury(0), it is likely that any effect a ligand might have on the $E_{1/2}$ value of the V^{IV}-V^{III} couple will be paralleled for the Hg^{II}-Hg^0 couple. Thus the observed correlation between the two half-wave potentials (see Table I) is not unexpected.

Half-wave potentials for the first reduction step of complexes with four-membered vanadium–dithio chelate ring systems became more negative in the order dadtp > dtcac > axan > mdtc ~ μ-dmebdtc ~ dadtc > cdtc. If the electron-donor capacities of the various chelates are important, a larger ligand to metal charge donation should stabilize the more electropositive vanadium(IV) system (d^1) in preference to the vanadium(III) system (d^2). Such an effect should lead to $E_{1/2}$ values generally occurring at more negative potentials, and in fact the above series shows that the ease of reduction correlates quite well with the amount of charge donated. The relative difficulty in reducing $[(cp)_2V^{IV}(cdtc)]^0$ is readily explicable in terms of the extra electron density on the sulfur atoms of the cdtc ligand, which is a dianion in its uncoordinated state. Similarly, the significant contribution made to the electronic structure of dithiocarbamates by canonical form c will also result in a higher electron density on the sulfurs
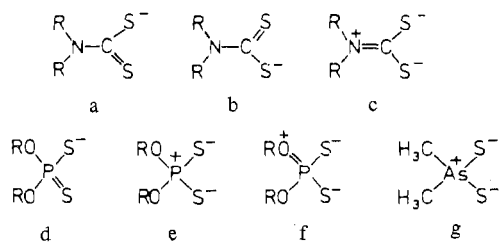
and thereby justify the position of dithiocarbamates in the above series. Equivalent forms are considered to be of lower importance in the other 1,1-dithiolates, and thus the degree of ligand to metal π bonding is lowered.

The negative inductive effect (−I) of *O*-alkyl groups on dialkyl dithiophosphates should stabilize canonical form d, rather than e or f, whereas the +I effect of the methyl groups on the dithiocacodylate ligand should favor form g rather than alternative forms. Thus on these grounds at least, the $[(cp)_2V(dtcac)]^+$ species should be harder to reduce.

Half-wave potentials for the reduction of complexes with 1,3-dithiolates were intermediate between those of the xanthates and dithiocarbamates (see Table I). The dithiobiuret complex was easier to reduce than the *O*-ethyl thioacetothioacetate derivative, perhaps indicating greater delocalization of charge over the dtb ligand backbone. The 1,2-dithiolate, $[(cp)_2V(mnt)]^0$, was the second most difficult compound to reduce. This undoubtedly results from the fact that it is a dianionic ligand; however some charge delocalization is expected over the vanadium–chelate ring system. In making comparisons between 1,1-, 1,2-, and 1,3-dithiolates, it should be mentioned that changing the size of the metal–chelate ring could have a substantial effect on the electronic structure of the various complexes and therefore also affect the ease of metal reduction.

Other studies[8,17] have shown that replacing sulfur donor

atoms on a chelate by oxygen donors generally renders reduction more difficult. This may be related to the greater ability of the sulfur donors to stabilize the lower oxidation state of a metal by their more extensively delocalized π systems. The dioxo chelates studied here were generally reduced at relatively negative potentials, although a direct comparison with the dithio chelates is not possible because of the different electronic and structural factors involved. However, the complexes with OEtSacSac and $S_1(acac)_2$ were quite similar in these respects, and the dioxo chelate complex was reduced at a more negative potential.

Vanadium(IV) is generally regarded as a class "a" metal[18] and therefore should form its most stable complexes with ligands coordinating through oxygen donor atoms. Although it has been shown that the characteristics of vanadium(IV) are modified by π-bonded cyclopentadienyl groups, the greater stability of our vanadium(III) dioxo chelates toward oxygen (as compared to the dithio chelates) indicates that the V^{III}-O bonds are stronger than the V^{III}-S ones.

No distinctive substituent effect was apparent for the dialkyldithiocarbamate and dialkyl dithiophosphate series, although the substituted chlorine on $de_{Cl}dtp$ made reduction easier than it was for the dedtp derivative. As mentioned above, the dithiophosphate complexes exhibit considerable dissociation, and thus the half-wave potentials from this series will differ from the $E°(V^{IV}$-$V^{III})$ values to an extent depending on the value of k_f. Variations from this source could quite easily mask any substituent effects. Similarly, the vanadium(III) complexes with dmdtc and dedtc were also prone to slight dissociation. Step C was only discernible in the case of the methyl derivative for the alkyl xanthate series, and interestingly the half-wave potentials became more negative as the length of the alkyl chain increased. This is possibly due to an increasing inductive effect.

The large difference between the $E_{1/2}$ values for the salicylaldehyde and acetylphenol complexes is surprising considering that the only difference between the chelates is the replacement of a hydrogen atom by a methyl group. Although the respective substituents are only one atom removed from the oxygen donor, the shift is too large to arise simply from an inductive effect.

Reduction with Sodium Amalgam. The existence of the neutral $[(cp)_2V(chelate)]^0$ complexes has been unambiguously demonstrated by polarographic measurements. However, the chemical synthesis of these complexes would prove a particularly arduous task in most cases because of their extreme sensitivity to oxygen. Moreover, the instability of some of these species even in the absence of oxygen virtually precludes the possibility of their isolation from acetone at room temperature.

In previous work, no evidence could be obtained for the formation of the required species despite many attempts to prepare them using controlled-potential electrolysis at platinum sheet, tungsten wire, and mercury pool electrodes.[4] Synthetic attempts were therefore made using chemical reducing agents. If an amalgam is used for the reduction, the progress of the reaction may be conveniently followed polarographically by inserting a dme into the reaction flask and thereby monitoring the increasing anodic component to wave 1. If the only change in the polarogram is the increasing anodic component of the wave, then the neutral vanadium(III) complex is most likely to be isostructural with the cationic vanadium(IV) species. Furthermore, if this occurs,

(17) A. R. Hendrickson, Ph.D. Thesis, University of Melbourne, 1973.

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

the $[(cp)_2V^{III}(chelate)]^0$ must be kinetically inert as regards dissociation. When the wave is purely anodic, the reaction is complete. The mercury added to the system during the experiment simply dilutes the amalgam and does not alter the system being measured.

Initially, a zinc–mercury amalgam seemed the best choice of reductant since the Zn^{2+}–Zn(amalgam) couple has an $E_{1/2}$ value of $\sim$−0.95 V (*i.e.*, more negative than the first reduction step for vanadium(IV) but more positive in most cases than subsequent reduction steps). However polarographic studies with $Zn(NO_3)_2$ showed that the couple is nonreversible in acetone.[19] The wave was drawn out and split, and the associated process is presumably complicated by kinetic factors. When the amalgam was placed in acetone solutions of some of the vanadium(IV) complexes, no reduction occurred (as shown by the zero anodic component of polarographic wave 1. The Na^+–Na(amalgam) couple gave a reversible polarographic wave in acetone at −1.74 V, and thus a sodium–mercury amalgam was next tested as a possible chemical reducing reagent.

An acetone solution of $[(cp)_2V(dbdtc)][Ph_4B]$ was bubbled out with argon in the polarographic cell and the Na–Hg amalgam added. The dibutyl derivative was chosen because the polarography of this complex indicated that the $[(cp)_2V^{III}.(dbdtc)]^0$ species was the most stable of the vanadium(III) dithiocarbamates toward oxygen and showed no signs of dissociation in its absence. After 5 min the solution had changed from green to purple and polarographic wave 1 was completely anodic (see Figure 6); *i.e.*, all vanadium(IV) species had been reduced to vanadium(III). As the half-wave potential for the second reduction step of the complex was close to that of the sodium couple ($\sim$−1.74 V), the amalgam might be expected to cause further reduction and possible decomposition of the $[(cp)_2V(dbdtc)]$ moiety. However, anodic wave 1 was the same height as the original cathodic wave 1 and wave 2 remained cathodic throughout the experiment.

Similar observations were made from $[(cp)_2V(bxan)][BF_4]$. The solution changed from purple to green in this case and wave 1 became completely anodic after about 5 min. The second polarographic reduction wave for the complex had a half-wave potential of −1.4 V, and therefore the presence of the amalgam could conceivably have led to further reduction. The fact that wave 2 remained cathodic implies that kinetic factors are important in the associated process. Certainly polarographic data showed this process to be irreversible. The polarogram did not alter over a 40-min period, so presumably the vanadium(III) species is quite stable under argon. The complex decomposed immediately when oxygen

(19) A. M. Bond, A. R. Hendrickson, and R. L. Martin, *J. Amer. Chem. Soc.*, **95**, 1449 (1973).
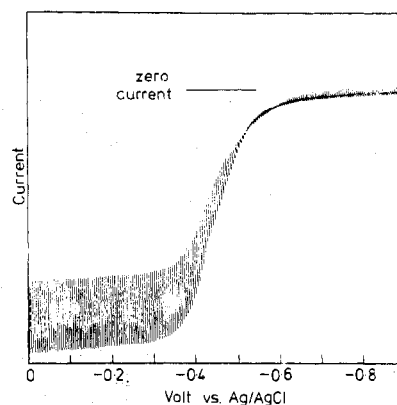

Figure 6. Dc anodic wave 1 from $[(cp)_2V(dbdtc)]^0$ species produced by reduction of the $[(cp)_2V^{IV}(dbdtc)]^+$ cation with the Na–Hg amalgam.

was allowed to enter the system, as would be expected from the polarographic studies.

Reduction of the $[(cp)_2V(dbdtc)][Ph_4B]$ complex was also followed by spectroscopy. No esr signals were obtained[16] from the reduced form of this complex, which is consistent with the result expected from vanadium(III) species in a tetragonally distorted tetrahedral field. In visible spectra, a new distinct band grew at 18,600 cm^{-1} (*cf.* the vanadium(IV) spectrum which showed only shoulders at 16,100 and 18,500 cm^{-1}, respectively, on the side of a charge-transfer band). Unfortunately, little is known about the spectra of the compounds and thus the significance of the observation remains uncertain.

Vanadium(III) dioxo chelates and $[(cp)_2V(oxine)]^0$ appeared quite stable on the polarographic time scale, even in the presence of oxygen. However, instead of producing an anodic current, wave 1 disappeared for all these complexes upon addition of the Na–Hg amalgam. This indicates that initially produced $(cp)_2V^{III}(chelate)$ species undergo additional reduction and/or chemical decomposition steps.