

Contribution from the Department of Chemistry,
University of California, Riverside, California 92502**Electrochemical Studies of Vanadium(III), -(IV), and -(V) Complexes of Diethyldithiocarbamate in Acetonitrile**

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The electrochemistry of $V(dtc)_3$, $VO(dtc)_2$, and $VO(dtc)_3$ ($dtc =$ diethyldithiocarbamate) has been studied by cyclic voltammetry and controlled-potential coulometry in acetonitrile at a platinum electrode. $V(dtc)_3$ is reversibly reduced by a 1-electron process at -1.075 V vs. SCE and is irreversibly oxidized at $+0.375$ V to both $V(IV)$ and $V(V)$ product species. $VO(dtc)_2$ is reduced at -1.35 V to an electroinactive $V(III)$ species as the major product and $V(dtc)_3$ as a minor product. $VO(dtc)_3$ is reduced to $VO(dtc)_2$ at -0.90 V with its subsequent electrochemical behavior the same as that for $VO(dtc)_2$. A comparison of the redox properties of these complexes with those of the analogous 8-quinolinol complexes has been made to evaluate ligand effects.

In recent electrochemical studies of metal complexes as models for metalloenzymes, molybdenum^{1,2} and vanadium³ complexes of 8-quinolinol have been considered as models for xanthine oxidase. Due to the extensive presence of inorganic sulfide in several molybdenum-containing enzymes, sulfur ligands also are of interest. The dithiocarbamates are good complexing ligands and provide a more electron-rich environment than 8-quinolinol. This has led to a recent electrochemical study of the molybdenum diethyldithiocarbamate complexes,⁴ with comparisons made between the 8-quinolinol and dithiocarbamate complexes.

The present work represents an extension of these model studies and involves the electrochemistry of vanadium diethyldithiocarbamate complexes in acetonitrile. Comparison of this ligand system with the 8-quinolinol system should provide a better understanding of vanadium oxidation-reduction chemistry in biological systems. Also, a comparison of the electrochemistry of the vanadium complexes with that of the analogous molybdenum complexes has been made. These studies have been carried out in an aprotic solvent in the belief that it is more representative of a biological environment. The water in the biological matrix is extensively modified through hydrogen bonding to protein and lipid fragments.⁵

Experimental Section

Cyclic voltammetric measurements were made with a three-electrode potentiostat constructed with solid-state operational amplifiers.⁶ The voltammograms were recorded on a Hewlett-Packard Moseley Model 7030A X-Y recorder. A Wenking Model 61RH potentiostat was used for controlled-potential electrolysis with current-time curves recorded by a Sargent Model SR strip-chart recorder. All electrochemical measurements were made inside a Vacuum Atmosphere Corp. Dri-Lab glove box filled with purified nitrogen.

The working electrode for cyclic voltammetry was a Beckman platinum-inlay electrode. For the controlled-potential electrolyses a platinum mesh electrode was used. The auxiliary electrode was a smaller piece of platinum mesh, separated from the cell solution by a fine porosity frit. The reference electrode consisted of a $Ag|AgCl$ electrode in aqueous tetramethylammonium chloride whose concentration was adjusted to make the electrode potential 0.000 V vs. SCE. The electrode had a small soft-glass cracked-bead tip and was placed inside a Luggin capillary in the cell assembly.

Reagents. Spectroquality acetonitrile (Matheson Coleman and Bell) was found to contain no significant electrochemically active impurities. The water content was below 0.03% (supplier's specifications) and was analyzed to contain less than 0.01% by other workers.¹⁶ Therefore, the solvent was used as received.

Tetraethylammonium perchlorate (TEAP) was used as supporting electrolyte and was prepared as described previously.³

Preparation of Complexes. (1) *Tris(N,N-diethyldithiocarbamate)vanadium(III)*. The only previously reported synthesis of the compound⁷ involved the addition of carbon disulfide to $V[N(C_2H_5)_2]_4$. For the present study a simpler synthesis was used, which was based on that for the dibenzyl and methylphenyl dithiocarbamate derivatives.⁸

In a nitrogen atmosphere drybox 2.7 g (11.5 mmol) of $Na(dtc)\cdot 3.5H_2O$ (Sigma Chemicals) was dissolved in 50 ml of degassed absolute ethanol. To this solution was added 0.59 g (3.75 mmol) of VCl_3 (Alfa Inorganic Chemicals); a bright orange-brown precipitate was collected and washed with ethanol. The identity of the compound was confirmed by its ir spectrum.⁷

(2) *Oxobis(N,N-diethyldithiocarbamate)vanadium(IV)*. This compound was made by adding 0.80 g (4 mmol) of $VOSO_4\cdot 2H_2O$ (BDH Chemicals) to an aqueous ethanol solution of 1.9 g (8.1 mmol) of $Na(dtc)\cdot 3.5H_2O$.⁹

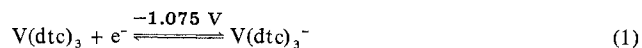
(3) *Oxotris(N,N-diethyldithiocarbamate)vanadium(V)*. This compound was prepared by adding 2.75 g (11.75 mmol) of $Na(dtc)\cdot 3.5H_2O$ to an aqueous solution of 0.78 g (3.9 mmol) of $VOSO_4\cdot 2H_2O$, which had previously been oxidized to vanadium(V) by hydrogen peroxide. The orange solid was extracted into chloroform and precipitated from excess ethanol.¹⁰

The composition and purity of these compounds was confirmed by elemental analyses, infrared spectra, and cyclic voltammetry.

Results and Discussion

$V^{III}(dtc)_3$. The cyclic voltammogram for a 1 mM solution of $V(dtc)_3$ (Figure 1a) exhibits a cathodic couple at -1.075 V vs. SCE and an anodic couple at $+0.35$ V. In both cases the anodic and cathodic peak-potential separations are near the theoretical value of 0.059 V for a reversible 1-electron process. For both couples the ratio of anodic to cathodic peak heights is unity, as expected for a reversible process.

The coulometric data from controlled potential reduction at -1.30 V indicate that the reduction is a 1-electron process. An anodic scan of the product solution yields the -1.05 V oxidation peak. A subsequent controlled potential oxidation at -0.90 V is a 1-electron process and results in the reappearance of the original reduction peak for an initially cathodic scan. This cyclic voltammogram is essentially identical with the initial one (Figure 1a), except that the reduction peak of the $+0.35$ -V couple is considerably smaller. These results indicate that the electrochemical step is



An initially anodic scan is identical with the cathodic scan shown in Figure 1a. The electrochemical step for the $+0.35$ V oxidation can be formulated as



but the appearance of a reduction peak at -0.10 V indicates that a subsequent chemical reaction gives at least one additional product. The cyclic voltammogram of a 0.25 -mM solution of $V(dtc)_3$ (Figure 1b) indicates that the reduction peak of the $+0.35$ -V couple is almost negligible at this lower concentration, but that significant reduction peaks are observed at -0.10 and -1.35 V. These latter peaks are visible in the cyclic voltammogram for a 1 -mM solution, but are negligible in the cyclic scan for a 5 -mM solution. Although the $+0.35$ -V

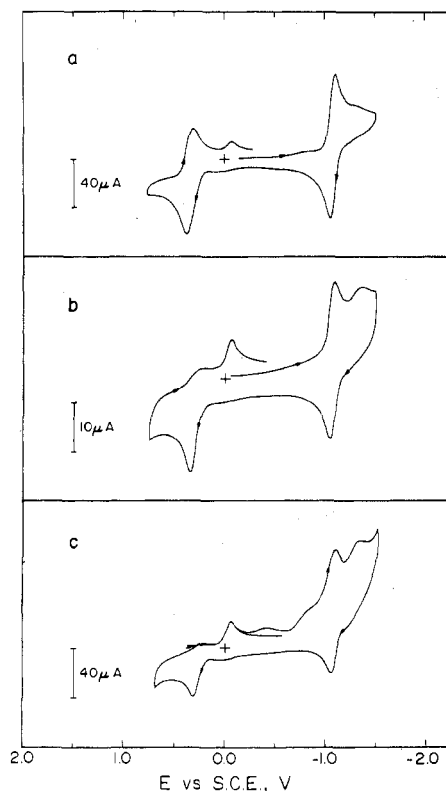
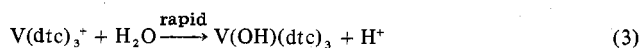


Figure 1. Cyclic voltammograms of (a) 1 mM $V(dtc)_3$, (b) 0.25 mM $V(dtc)_3$, and (c) 1 mM $V(dtc)_3$ after controlled-potential oxidation at +0.50 V. All solutions contain 0.1 M TEAP in acetonitrile; scan rate, 0.2 V/s.

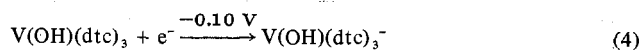
couple is essentially irreversible for the 0.25-mM solution, it is the dominant reaction for a 1-mM solution, and the only reaction for a 5-mM solution. Thus, the system appears simple at the higher concentrations, but at 0.25 mM, oxidation at +0.375 V leads to at least three products.¹¹

Coulometric data for the controlled-potential oxidation of $V(dtc)_3$ at +0.50 V, although not conclusive, indicate that the primary electrochemical step is represented by eq 2. This conclusion is further supported by the observation that the ratio of the cathodic to anodic peak currents for the +0.35 V couple approaches unity with increasingly rapid scan rates.

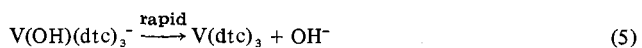
The cyclic voltammogram that is observed after controlled potential oxidation of $V(dtc)_3$ at +0.50 V is essentially the same for all three concentrations; that for the 1 mM solution is shown in Figure 1c. For the initial scan a reduction peak is not observed at +0.325 V, which indicates that the $V(dtc)_3^+$ species is not stable. When a small amount of water is added to a solution of $V(dtc)_3$ the +0.35-V oxidation is not reversible, which indicates that $V(dtc)_3^+$ reacts rapidly with water. Thus, $V(dtc)_3^+$ produced by controlled-potential oxidation apparently is hydrolyzed by residual water in the solvent (eq 3). The



resultant species, $V(OH)(dte)_3$, is reduced at -0.10 V.



(Proton reduction is responsible for the reduction peak at -0.40 V.) The reduction product (eq 4) quickly dissociates to give the initial tris complex



and a reversible couple at -1.075 V.

On the basis of the data in later sections, the reduction peaks at -0.90 and -1.35 V are believed to be due to $VO(dtc)_3$ and

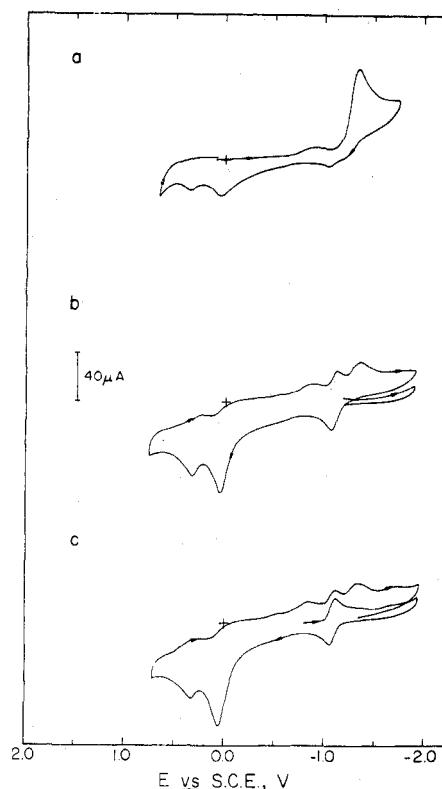
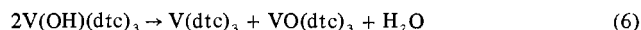
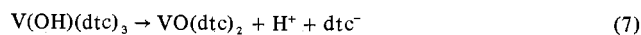


Figure 2. Cyclic voltammograms of (a) 1 mM $VO(dtc)_2$, (b) solution (a) after controlled-potential reduction at -1.50 V, and (c) solution (b) after 1 h. All solutions contain 0.1 M TEAP in acetonitrile; scan rate, 0.2 V/s.

$VO(dtc)_2$, respectively. To account for these species in Figure 1c, $V(OH)(dte)_3$ probably undergoes two reactions in addition to that given by eq 4. A disproportionation reaction would account for the $VO(dtc)_3$ peak



and, when considered with eq 5, indicates why the $V(dtc)_3$ reduction peak is larger than that for $VO(dtc)_3$. The $VO(dtc)_2$ species probably is produced by a dissociation reaction



and accounts for the reduction peak at -1.35 V.

On a second cyclic scan a small reduction peak at +0.325 V is observed because some $V(dtc)_3$ has been regenerated and then oxidized at +0.375 V. A proton reduction peak is not seen on the second cycle.

The relative peak heights for the reductions at -0.90, -1.075, and -1.35 V (after anodic electrolysis) vary with the concentration of $V(dtc)_3$, which indicates the relative dominance of the reactions that compete for the product species, $V(OH)(dte)_3$. However, within 10 min after controlled-potential oxidation is complete for all concentrations, the reduction peak for $V(OH)(dte)_3$ at -0.10 V has disappeared.

$V^{IV}(dte)_2$. The electrochemical behavior of $VO(dtc)_2$ is illustrated by Figure 2a. The reduction at -1.35 V is believed to be due to the vanadium(IV) \rightarrow vanadium(III) couple, with the small pre-wave at -0.90 V probably due to a vanadium(V) reduction. On the basis of electrochemical studies of the diethyldithiocarbamate anion, the anodic peak at +0.05 V is due to a ligand oxidation process



On the basis of the preceding discussions, the oxidation peak at +0.375 V is due to $V(dtc)_3$. Because an initial anodic scan does not yield any oxidation peaks, a small amount of both

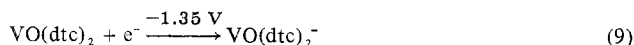
$V(dtc)_3$ and dtc^- must result from the $VO(dtc)_2$ reduction process.

The controlled-potential reduction of $VO(dtc)_2$ is not accomplished easily. Coulometry at a control potential of -1.50 V does not appear to reduce the solution; that is, only a small number of coulombs is passed and a cyclic voltammogram for the resulting solution is not significantly different from that of Figure 2a.

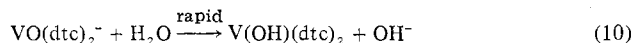
However, the rest potential has shifted to about -0.50 V and the -0.90 -V reduction peak has disappeared. An anodic scan indicates that free ligand is present in the solution (oxidation peak at $+0.05$ V), but there is no evidence for $V(dtc)_3$. The same results are obtained when the first controlled-potential reduction is carried out at -1.00 V.

A second controlled-potential reduction of the same solution at a potential of -1.50 V results in the cyclic voltammogram shown in Figure 2b.¹² There are not any cathodic peaks present initially, but an oxidation peak is observed at -1.05 V which corresponds to the reverse of eq 1. The oxidation peak at $+0.05$ V is due to dtc^- (eq 8) and that at $+0.375$ V corresponds to $V(dtc)_3$ (eq 2). On the reverse scan, the reductions at -0.90 , -1.10 , and -1.35 V correspond to a vanadium(V) species, $V(dtc)_3$, and $VO(dtc)_2$, respectively.

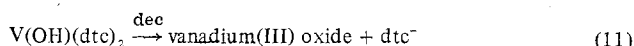
The oxidation peak for $V(dtc)_3^-$ that is observed on the initial scan after coulometric reduction of $VO(dtc)_2$ indicates that the latter species has been reduced by two electrons. However, the coulometric data indicate a 1-electron process and the height of the $V(dtc)_3^-$ oxidation peak does not account for all of the vanadium present. Thus, the primary reduction is believed to be a one-electron process



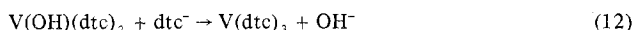
with $VO(dtc)_2^-$ undergoing a rapid hydrolysis



Most of the $V(OH)(dte)_2$ then decomposes to an electroinactive vanadium(III) oxide (because no new oxidation peak is observed) and free ligand



The remaining fraction of $V(OH)(dte)_2$ undergoes an exchange reaction with free ligand to form $V(dtc)_3$



At a control potential of -1.50 V the resultant $V(dtc)_3$ is spontaneously reduced to $V(dtc)_3^-$ (eq 1), but its limited amount does not affect the coulometry significantly.

After the oxidation of $V(dtc)_3^-$ to $V(dtc)_3$ at -1.05 V and of $V(dtc)_3$ to $V(dtc)_3^+$ at $+0.375$ V, the reactions represented by eq 3–7 probably occur and account for the three reduction peaks at -0.90 , -1.10 , and -1.35 V of the cyclic voltammogram.

Within 5 min after the coulometric reduction of $VO(dtc)_2$ at -1.50 V, the cyclic voltammogram of the product solution begins to change. The rest potential shifts to more positive values and $V(dtc)_3^-$ is oxidized to $V(dtc)_3$. Within an hour after the coulometric reduction the cyclic voltammogram is represented by Figure 2c. The rest potential has shifted to -0.80 V and a reduction peak for $V(dtc)_3$ appears on an initial cathodic scan. After 18 h the rest potential is at -0.60 V and most of the vanadium is present as $VO(dtc)_2$. The cyclic voltammogram for the latter solution is essentially the same as that for a $VO(dtc)_2$ solution (Figure 2a), except that the $VO(dtc)_2$ reduction peak is smaller and the dtc^- oxidation peak is larger. The cause of these spontaneous oxidations and the nature of the corresponding reductions is not clear from the electrochemical data.

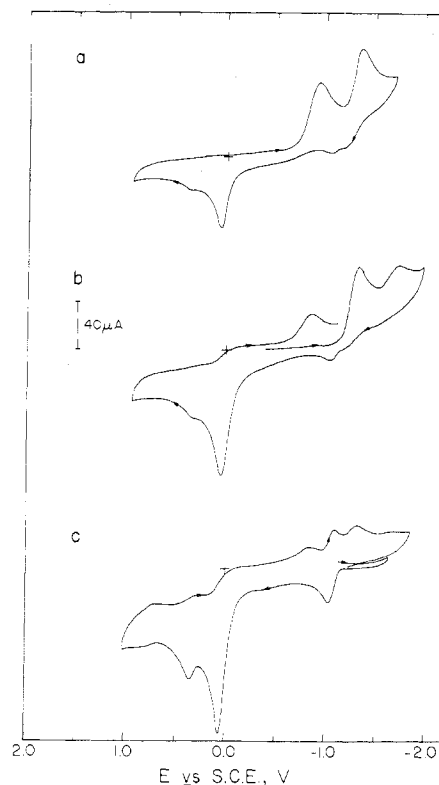
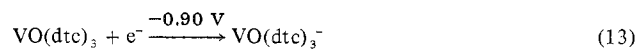


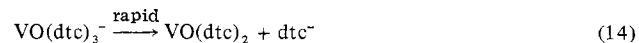
Figure 3. Cyclic voltammograms of (a) 1 mM $VO(dtc)_3$, (b) solution (a) after controlled-potential reduction at -1.10 V, and (c) solution (b) after controlled-potential reduction at -1.50 V. All solutions contain 0.1 M TEAP in acetonitrile; scan rate, 0.2 V/s.

$VVO(dtc)_3$. The cyclic voltammogram of $VO(dtc)_3$, which is illustrated by Figure 3a, includes irreversible reductions at -0.90 and -1.35 V for an initial cathodic scan. The -0.90 -V reduction is believed to be due to a vanadium(V) \rightarrow vanadium(IV) couple and that at -1.35 V to be due to $VO(dtc)_2$ (eq 9). An initial anodic scan does not include any oxidation peaks. Hence, the dtc^- oxidation peak at $+0.05$ V must result from the initial reductions. Comparison of scans that are reversed after the first and second reduction peaks indicates that the oxidation peak at $+0.05$ V is considerably larger after the more negative cathodic scan. Thus, dtc^- is released by both reduction reactions.

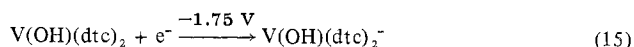
Controlled-potential electrolysis at -1.10 V yields a solution with the cyclic voltammogram that is illustrated by Figure 3b. The coulometric data indicate that the reduction is a 1-electron process and an initial anodic scan of the product solution confirms that free dtc^- is present. The reduction process appears to involve a primary electron-transfer reaction



that is followed by a rapid ligand dissociation reaction.



The species responsible for the -1.75 -V reduction peak is uncertain. After the reduction of $VO(dtc)_2$ and the subsequent hydrolysis of the product (eq 9 and 10), $V(OH)(dte)_2$ may be reduced.

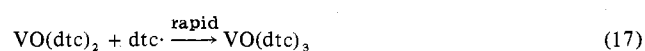


Because a new oxidation peak is not observed with a reverse scan, $V(OH)(dte)_2^-$ or the product of a further chemical reaction is electroinactive.

Although there is not an obvious oxidation peak that can be assigned to a vanadium(IV) \rightarrow vanadium(V) reaction

during a reverse anodic scan, this reaction must occur because the second scan of a cyclic voltammogram indicates that the -0.90-V reduction peak reappears. Variation of the positive potential limit for a series of cyclic voltammograms (initial negative scan) establishes that when the anodic scan is reversed before the $+0.05\text{-V}$ oxidation peak, a reduction peak at -0.90 V is not observed on the second cycle. When the anodic scan is reversed after the $+0.05\text{-V}$ oxidation peak, the -0.90-V reduction peak is observed.

An initial cathodic scan of a solution equimolar in $\text{VO}(\text{dte})_2$ and $\text{Na}(\text{dte})$ yields a negligible reduction peak at -0.90 V , while an initial anodic scan exhibits a large reduction peak at -0.90 V on the reverse scan. After controlled potential oxidation of the dte^- ligand at $+0.30\text{ V}$ an initial cathodic scan yields the large reduction peak at -0.90 V . Thus, oxidized ligand combines with $\text{VO}(\text{dte})_2$ to form the vanadium(V) complex. Recasting equation 8 to indicate the formation of a radical, the probable reactions are



A second controlled-potential electrolysis, at -1.50 V , yields a solution with the cyclic voltammogram shown in Figure 3c. This cyclic is essentially identical with that for the electrolysis reduction product of $\text{VO}(\text{dte})_2$ (Figure 2b), except that more free ligand is present when the initial solution is $\text{VO}(\text{dte})_3$. The coulometric data again indicate a one-electron process and the interpretation is as before; most of the vanadium becomes an electroinactive vanadium(III) oxide with a small amount reduced to $\text{V}(\text{dte})_3^-$. With time the rest potential shifts anodically as $\text{V}(\text{dte})_3^-$ is oxidized to $\text{V}(\text{dte})_3$, but even after 20 h the oxidation process does not yield $\text{VO}(\text{dte})_2$.

Conclusions

Although a previous comparison of vanadium and molybdenum 8-quinolinol coordination chemistries has indicated some similarities,³ a comparison of vanadium and molybdenum dithiocarbamate coordination chemistries shows fewer similarities than expected. Molybdenum dithiocarbamate coordination chemistry⁴ includes a strong tendency for formation of dioxo-bridged binuclear dimers and the presence of dimer-tetramer equilibria. The present study has not yielded any evidence for mono- or dioxo-bridged binuclear dimers, although they are known with other ligands.^{3,13} Complexes of the higher oxidation states of molybdenum usually include one or two terminal oxygen atoms, whereas vanadium complexes have at most one terminal oxygen atom. The most common coordination number for both vanadium and molybdenum complexes is six, but complexes with higher coordination numbers are known for both metals. The coordination number is seven for compounds such as $[\text{VO}(\text{dte})_3]^{7,10}$ and $[\text{Mo}_2\text{O}_4(\text{dte})_4]^{4,14}$ and is eight for $[\text{V}(\text{dte})_4]^{7,14}$ and $[\text{Mo}(\text{dte})_4]^+$.

More useful than the above comparisons is an evaluation of ligand effects on vanadium oxidation-reduction potentials and the chemistry of its various oxidation states (see Table I). For the $3+$ oxidation state the electrochemistry of vanadium 8-quinolinol and dithiocarbamate complexes is similar. Both $\text{V}(\text{dte})_3$ and VQ_3 (Q , 8-quinolinol anion) are reversibly reduced by a one-electron process at -1.075 and -1.475 V , respectively. Both are irreversibly oxidized by a 1-electron process at $+0.35$ and $+0.45\text{ V}$, respectively. In each case several products are formed, with at least one of them analogous to the stable vanadium(IV) complex ($\text{VO}(\text{dte})_2$ or VOQ_2).

The electrochemical data establish that $\text{V}(\text{dte})_3$ is easier to reduce and to oxidize than VQ_3 . This probably is due to the

Table I. Comparison of Oxidation and Reduction Potentials of Vanadium Dithiocarbamate and 8-Quinolinol Complexes in Acetonitrile

Complex	Potentials, V vs. SCE ^d	
	Reduction	Oxidation
$\text{V}(\text{dte})_3$	-1.075 R	$+0.35\text{ I}$
VQ_3^a	-1.475 R	$+0.45\text{ I}^b$
$\text{VO}(\text{dte})_2$	-1.35 I	
VOQ_2^a		$+0.775\text{ I}$
$\text{VO}(\text{dte})_3$	-0.90 I	
$\text{VO}(\text{OCH}_3)_2\text{Q}_2^a$	-0.40 I^b	
$\text{VO}(\text{OH})\text{Q}_2^a$	-0.05 R^c	

^a Reference 3. ^b Reversible on the cyclic voltammogram time scale. ^c Reversible with the $\text{V}(\text{IV-V})$ dimer. ^d R = reversible; I = irreversible.

greater electron density and/or electron mobility in the dithiocarbamate ligand.

The vanadium(IV) complexes, $\text{VO}(\text{dte})_2$ and VOQ_2 , have quite different electrochemical properties. $\text{VO}(\text{dte})_2$ is reduced to a vanadium(III) oxide (perhaps V_2O_3), while reduction of VOQ_2 is not possible. The reduction of $\text{VO}(\text{dte})_2$ is complicated and includes the formation of a small amount of $\text{V}(\text{dte})_3$. On the other hand, the VOQ_2 complex is oxidized to $\text{VO}(\text{OH})\text{Q}_2$ and/or $(\text{VOQ}_2)\text{-O-}(\text{VOQ}_2)$, while $\text{VO}(\text{dte})_2$ is not oxidizable.

The vanadium(V) complexes have different coordination numbers, and consequently quite different electrochemical properties. The electron-rich nature of the dithiocarbamate ligands causes them to bind tightly enough to overcome steric repulsions and form a stable seven-coordinate complex, $\text{VO}(\text{dte})_3$. The 8-quinolinol complexes are six coordinate: $\text{VO}(\text{OCH}_3)_2\text{Q}_2$ and $\text{VO}(\text{OH})\text{Q}_2$ as monomers, or $(\text{VOQ}_2)\text{-O-}(\text{VOQ}_2)$ as a dimer.^{3,15} Reduction of $\text{VO}(\text{dte})_3$ gives $\text{VO}(\text{dte})_2$ and free ligand, while reduction of either of the vanadium(V)-8-quinolinol complexes gives a (IV-V) dimer, $[(\text{VOQ}_2)\text{-O-}(\text{VOQ}_2)]^-$.

Although these compounds cannot at present be related to specific biological systems, the ligand effects clearly are large, both in terms of the oxidation-reduction chemistry and the coordination chemistry. Sulfur-containing ligands appear to enhance redox reactions in the lower oxidation states of vanadium, while the 8-quinolinol ligand appears to provide a better coordination sphere for reversible oxidation-reduction reactions of higher oxidation state complexes.

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Registry No. $\text{V}(\text{dte})_3$, 51684-55-0; $\text{VO}(\text{dte})_2$, 15283-34-8; $\text{VO}(\text{dte})_3$, 36464-03-6.

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- (11) Although the -1.35-V reduction peak is observed for an initial cathodic scan, the peak height is enhanced on consecutive cyclic scans. This implies that the species reduced at -1.35 V is also a product of the $+0.375\text{-V}$ oxidation.
- (12) Because the first coulometric reduction produced free dte^- , excess ligand was believed to be necessary for $\text{VO}(\text{dte})_2$ to be reduced. However, addition of $\text{Na}(\text{dte})$ to the electrolysis solution at various times during

- a coulometric study established that excess free ligand did not enhance the reduction process.
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Chemistry of *trans*-Aquanitrosyltetraammine technetium(II) and Related Studies

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Attempts to reduce Tc(VII) or Tc(IV) in strongly acidic solutions containing noncomplexing anions indicate that reduction to Tc(II) is possible, but the species of lower oxidation state are unstable and there is no assurance that they are mononuclear. This instability contrasts markedly with that of a compound reported by Eakins et al.² as containing $[\text{Tc}(\text{NH}_2\text{OH})_2(\text{NH}_3)_3\text{H}_2\text{O}]^{2+}$. Structure determination by Radonovich and Hoard on the chloride salt of the cation shows it to be *trans*- $[\text{Tc}(\text{NH}_3)_4(\text{H}_2\text{O})\text{NO}]^{2+}$, rather than that formulated by Eakins. The nitrosyl ion shows a stretch in the ir spectrum at 1680 cm^{-1} , the low frequency indicating great stabilization by $\text{Tc}^{1+} \rightarrow (\text{NO})^1$ back-bonding. The species is remarkably inert to substitution, as is the nitrosyl group to nucleophilic attack. At low pH, the *trans*- $[\text{Tc}(\text{NH}_3)_4(\text{H}_2\text{O})\text{NO}]^{3+/2+}$ couple is reversible, E° against NHE being 0.80 V. The ion of higher oxidation state undergoes substitution more readily than does that of charge 2+ and is unstable at higher pH. The values of $\text{p}K_a$ for the 2+ and 3+ species have been measured as 7.3 and ca. 2.0, respectively. Modification of the Eakins method of preparation leads to other derivatives but of these only $[\text{Tc}(1,10\text{-phen})_2(\text{NH}_3)\text{NO}]^{2+}$ has been at all well characterized.

Introduction

A large amount of interesting chemistry depends on the propensity which Ru(II), when most of the ligands in combination with it are saturated, has for back-bonding with an unsaturated one.¹ It was felt that Tc(II) in a similar state of combination would show the effects of back-bonding to an even greater degree than does Ru(II), and the original motivation for the work to be described was to prepare Tc(II) as a mononuclear complex having only saturated ligands associated with it. This part of the work led to failure even when very powerful reducing agents were used in water solution and will be reported on only very briefly. Our attention then turned to the investigation of a compound, reported² as having the composition $[\text{Tc}(\text{NH}_2\text{OH})_2(\text{NH}_3)_3\text{H}_2\text{O}]\text{Cl}_2$ (the cation is hereafter referred to as the pink ion or complex). If correctly formulated, this compound would in fact be an example of what we originally sought to prepare. The great stability of the compound was however in marked contrast to the instability our own experiments led us to assign to mononuclear Tc(II) in combination with saturated ligands. The major part of this report deals with characterizing the pink complex and developing its chemistry further.

Experimental Section

Materials. All stock solutions and aqueous reaction media were made up using doubly distilled water.

Argon as obtained from Liquid Carbonic was 97.95% pure. To remove oxygen, the gas was passed through two bubbling towers containing Cr(II). All-glass lines were used to convey it to reaction vessels.

Bio-Rad Ag50W-X2, 200–400 mesh cation-exchange resin was cleaned following the procedure described by Deutsch.³

Deuterium oxide (99.84 mol %) was purchased from Bio-Rad. Nitric oxide and dinitrogen were used as delivered from lecture bottles supplied by Matheson Co.

Trifluoromethanesulfonic acid as obtained from 3M Co. was redistilled and then diluted to 6 M for storage. Trifluoroacetic acid as purchased from Matheson Coleman and Bell and tetrafluoroboric acid as purchased from J.T. Baker were used without further purification.

Pyrazine, 2,2'-bipyridine, and 1,10-phenanthroline purchased from Aldrich were used without further purification. Pyridine was stored over molecular sieve. Isonicotinamide was purified by recrystallization from water.

Hydroxylamine hydrochloride and hydrazine hydrate (99–100%) were used as purchased from Matheson Coleman and Bell.

The reducing agents Cr^{2+} , V^{2+} , and Eu^{2+} were generated from Cr^{3+} , VO^{2+} , and Eu^{3+} as trifluoromethanesulfonate salts in trifluoromethanesulfonic acid using amalgamated zinc. The solution of $\text{Cr}^{3+}(\text{aq})$ was generated from CrO_3 dissolved in trifluoromethanesulfonic acid solution using H_2O_2 as reducing agent.⁴ The solution containing VO^{2+} was prepared as described by Deutsch.³ Europium(III) in solution was prepared by dissolving a known quantity of Eu_2O_3 (99.9% purity supplied by Grace Chemical Co.) in an excess of acid in aqueous solution.

Technetium-99, a weak β emitter with a half-life of 2.12×10^5 years⁵ was purchased from Oak Ridge National Laboratory, in two lots, one as solid ammonium pertechnetate and the other as a solution of the salt in 0.08 M acid. The salt $(\text{NH}_4)_2\text{TcCl}_6$ was prepared by a slight variation of the method of Nelson et al.⁶ and the hexaiodo salt by the method of Dalziel et al.⁷ The preparation of the pink compound of Eakins et al.² worked precisely as described by them. In addition to following the procedure outlined by them for obtaining a solid, a cation-exchange column was used to isolate a pink band. This band was eluted by 1 M HCl, the solution containing it was evaporated to dryness, and the solid was recrystallized from water and absolute ethanol. When the solid was dissolved in water and the resultant solution allowed to evaporate at room temperature, a crystalline product formed. Some of the crystals proved to be suitable for structural determination by x-ray diffraction. Eakins et al.² described the preparation only of the chloride salt of the pink complex. The bromide and tetrafluoroborate salts were prepared by dissolving the chloride in water, capturing the pink complex on a cation-exchange resin, eluting it with 1 M trifluoromethanesulfonic acid, and precipitating it by adding solid NaBr or concentrated HBF_4 . For the trifluoroacetate salt, 1 M trifluoroacetic acid was used as eluent, and the solid was obtained by rotary evaporation. In each case the solid was recrystallized from water and absolute ethanol.

The description of a number of other preparations which are not such obvious extensions of established procedures are deferred to the Results section.

Apparatus and Methods. Provision was made so that, when necessary, operations, including ion-exchange separations, were carried out under inert atmospheres.

UV and visible spectra were recorded on Cary 14 or 15 spectrophotometers. Infrared spectra were taken on a Perkin-Elmer Model 621 spectrophotometer covering the range $250\text{--}4000\text{ cm}^{-1}$, samples being pelleted in KBr.

The cyclic voltammetry apparatus was built by Glenn Tom. The reference electrode was saturated calomel and the indicator electrode