

Electrochemical Studies of Vanadium(III) and Vanadium(IV) Acetylacetonate Complexes in Dimethyl Sulfoxide

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The electrochemistry of $V(acac)_3$ and $VO(acac)_2$ ($acac^-$ = acetylacetonate anion) has been studied by cyclic voltammetry and controlled-potential coulometry in dimethyl sulfoxide at a platinum electrode. $VO(acac)_2$ is irreversibly reduced by one electron at -1.9 V vs. SCE to a stable V^{III} product. In the presence of excess ligand, $VO(acac)_2$ is reduced by two electrons to $V(acac)_3^-$, with the V^{III} species mentioned above and $V(acac)_3$ as intermediates. $V(acac)_3$ is reversibly reduced to $V(acac)_3^-$ at -1.42 V. The one-electron oxidation of $VO(acac)_2$ and the two-electron oxidation of $V(acac)_3$ (at $+0.81$ and $+0.76$ V, respectively) give the same vanadium(V) product. The reduction products of this species depend on whether or not free ligand is present.

Introduction

Although a wide range of effects of vanadium on biological systems has been reported and its essentiality for some animals has been demonstrated, its function on a molecular level is obscure.¹ Its similarity to molybdenum (essential for the activity of enzymes such as xanthine oxidase, aldehyde oxidase, and nitrogenase) suggests that vanadium may function as a metalloenzyme. On this basis fundamental electrochemical studies of vanadium in the high oxidation states have been started. Initial work has been carried out on complexes with bidentate ligands bonding through oxygen and nitrogen atoms (8-hydroxyquinoline)² and two sulfur atoms (diethyldithiocarbamate).³

The present work is an extension of these fundamental studies and involves the electrochemistry of vanadium acetylacetonate (2,4-pentanedione) complexes in dimethyl sulfoxide. The use of aprotic solvents has been discussed previously.² A comparison of this ligand system to those reported earlier is made. Furthermore, these results are compared to those of Kitamura and co-workers⁴⁻⁶ regarding the reduction of vanadyl acetylacetonate in acetonitrile.

Experimental Section

Cyclic voltammetric measurements were made with a Princeton Applied Research Model 173 three-electrode potentiostat and a Model 175 Universal Programmer. The voltammograms were recorded on a Houston Instruments Model 2000 Omnigraphic X-Y recorder. Controlled-potential electrolysis was carried out with the above potentiostat and a Princeton Applied Research Model 179 digital coulometer.

The working electrode for cyclic voltammetry was a Beckman platinum-inlay electrode. A platinum mesh electrode was used for controlled-potential electrolysis. The auxiliary electrode was a small piece of platinum foil separated from the cell solution by a fine porosity frit. The reference electrode consisted of a Ag/AgCl electrode in aqueous tetramethylammonium chloride (Aldrich) with the concentration adjusted to make the electrode potential 0.000 V vs. SCE. The reference electrode junction was a small soft-glass cracked-bead sealed into a Pyrex tube. The electrode was positioned in a luggin capillary in the cell assembly.

Most experiments were carried out in an all-glass cell constructed from standard taper 60/50 inner and outer ground glass joints. The electrodes were positioned in the cell cap by means of several smaller

ground glass joints. Prepurified nitrogen was flushed through the cell during use, and a septum covered port allowed the removal of solution aliquots by syringe. Some coulometric measurements were done in a Vacuum Atmospheres Co. Model HE-43-2 glovebox with an HE 493 Dri-train, under a nitrogen atmosphere.

Spectrophotometric measurements were made on a Cary Model 14 UV-vis spectrophotometer.

Reagents. High-purity dimethyl sulfoxide and acetonitrile were obtained from Burdick and Jackson Laboratories with lot analyses for water of 0.01% and 0.003%, respectively. As no significant electrochemical impurities were found, these solvents were used as received.

Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium bromide (Aldrich) and perchloric acid as previously described² and was used as the supporting electrolyte. Tetraethylammonium hydroxide was obtained from Aldrich as a 25% solution in water.

Oxobis(2,4-pentanedionato)vanadium(IV) ($VO(acac)_2$, vanadyl acetylacetonate) was obtained from Alfa Products Co. and was recrystallized from chloroform. Tris(2,4-pentanedionato)vanadium (III) ($V(acac)_3$) was prepared by the method of Dilli and Patsalides.⁷

Results and Discussion

Reduction Processes. A 1 mM solution of $VO(acac)_2$ with TEAP in Me_2SO gives the cyclic voltammogram shown in Figure 1a. Two overlapping irreversible reduction peaks at -1.85 and -1.95 V are exhibited on an initial negative scan. The oxidation peak at $+0.25$ V is observed only after cathodic scanning of the two reduction peaks, while the oxidation at $+0.81$ V appears on an initial positive scan. Thus, the species oxidized at $+0.25$ V appears to be the major product of $VO(acac)_2$ reduction.

The reduction of $VO(acac)_2$ has been studied previously by two groups.^{4,8} The two reduction peaks at -1.85 and -1.95 V appear to coincide with a prewave and a major wave reported by Kitamura and co-workers.⁴ In their polarographic study of $VO(acac)_2$ in acetonitrile, half-wave potentials near -2.00 V were reported, measured with a Ag/AgClO₄ (0.1 M acetonitrile) reference electrode. Kitamura also found that a single distinct reduction process resulted when the experiment was carried out with a large excess of free ligand present. Thus, all further work by these researchers was done in the presence of a 20-fold excess of free ligand.

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(2) Riechel, T. L.; Sawyer, D. T. *Inorg. Chem.* **1975**, *14*, 1869.

(3) Riechel, T. L.; DeHayes L. J.; Sawyer, D. T. *Inorg. Chem.* **1976**, *15*, 1900.

(4) Kitamura, M.; Yamashita, K.; Imai, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 97.

(5) Kitamura, M.; Yamashita, K.; Imai, H. *Chem. Lett. J.* **1975**, 1071.

(6) Kitamura, M.; Sasaki, K.; Imai, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3199.

(7) Dilli, S.; Patsalides, E. *Aust. J. Chem.* **1976**, *29*, 2389.

(8) Gritzner, G.; Murauer, H.; Gutmann, V. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *101*, 177. The half-wave potential for the reduction of $VO(acac)_2$ was reported as -0.85 V vs. a bis(biphenyl)-chromium(I) reference electrode. It is thus difficult to compare this result to our value. The process was said to be irreversible, but no coulometric data was given. The authors also concluded that the limiting current for $VO(acac)_2$ reduction was kinetically controlled, but no further study of the system was made.

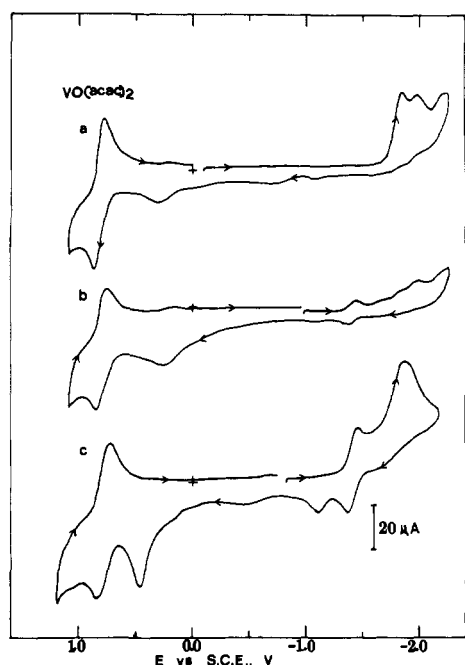
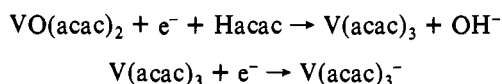


Figure 1. Cyclic voltammograms in 0.1 M TEAP/Me₂SO solution of (a) 1 mM VO(acac)₂, (b) solution a after reduction at -2.1 V, and (c) solution b with 6 mM Hacac added (scan rate 0.2 V/s).

Table I. Reactions Based on the Reductions of VO(acac)₂ and V(acac)₃

reaction	potentials, V vs. SCE		
	<i>E'</i>	<i>E</i> _{pc}	<i>E</i> _{pa}
(1) VO(acac) ₂ + e ⁻ → VO(acac) ₂ ⁻		-1.90	
(2) VO(acac) ₂ ^{rapid} → V ^{III}			
(3) V ^{III} → VO(acac) ₂ + e ⁻			+0.25
(4) V ^{III} + Hacac → V(acac) ₃			
(5) V(acac) ₃ + e ⁻ ⇌ V(acac) ₃ ⁻	-1.42		
(6) Hacac + e ⁻ → Hacac ⁻		-2.06	
(7) Hacac ⁻ → 1/2 H ₂ + acac ⁻			
(8) acac ⁻ oxidation			+0.44

Under these conditions, Kitamura concluded that the reduction process is irreversible and involves a two-electron transfer with V(acac)₃⁻ as its final product. His proposed mechanism is



An activated complex [V(acac)₂·O·Hacac]^{*} was postulated as an intermediate in the first step. Presumably, V=O bond breaking and ligand addition were thought to occur during the first reduction step. No data was presented to verify the identity of the V(acac)₃ and V(acac)₃⁻ species.

In the present work, the reduction of VO(acac)₂ has been studied both with and without free ligand present in order to clarify Kitamura's results.

The 1 mM solution of VO(acac)₂ discussed above (Figure 1a) was reduced by controlled-potential electrolysis at -2.1 V. The initial blue-green solution becomes black at the end of the reduction process, which the coulometric data indicate is a one-electron transfer. The cyclic voltammogram of the black solution (Figure 1b) shows that the anodic peak at +0.25 V has increased in size. Furthermore, an initial positive scan shows this peak on the first cycle, indicating that it is the primary reduction product. This product is most probably a V^{III} species but is not V(acac)₃. (The presence of a small amount of V(acac)₃ is indicated by the couple at -1.42 V and

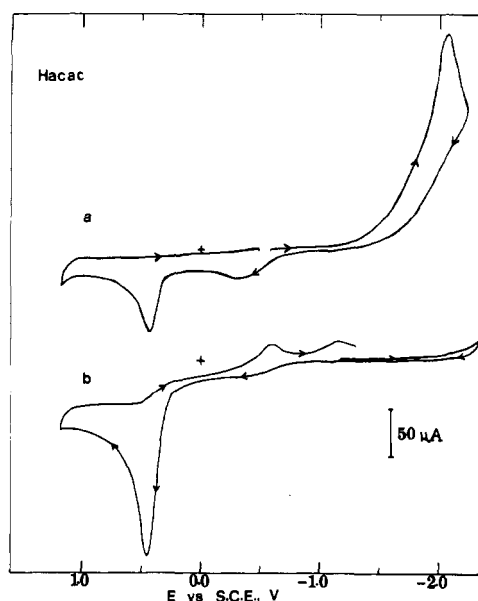


Figure 2. Cyclic voltammograms in 0.1 M TEAP/Me₂SO solution of (a) 6 mM Hacac and (b) solution a after reduction at -2.2 V (scan rate 0.2 V/s).

will be discussed later.) Subsequent oxidation of the V^{III} species produces some VO(acac)₂ but not quantitatively. Thus, for the reduction of VO(acac)₂ without free ligand present we propose reactions 1-3 in Table I.

When a sixfold excess of free ligand is added to the black solution (Figure 1b), the solution quickly changes to dark yellow which matches the color of V(acac)₃ in Me₂SO. A cyclic voltammogram of this solution is shown in Figure 1c. The reduction peak at -2.06 V and the oxidation peak at +0.44 V correspond to Hacac and acac⁻, respectively. These assignments are verified by Figure 2, which shows the voltammograms for Hacac (2a) and the subsequent reduction product (2b). The proposed reactions (Table I (6)-(8)) are based on similar equations presented by Neal and Murray.⁹ They reported the reduction of Hacac at -2.2 V vs. SCE using a mercury electrode in acetonitrile.

Of greater importance is the disappearance of the +0.25 V oxidation peak and the marked enhancement of the couple at -1.42 V. As will be discussed shortly, this couple corresponds to the reversible reduction of V(acac)₃. Thus, although Figure 1b indicates that a small amount of V(acac)₃ is formed during the initial reduction process, the intermediate V^{III} species is the major product, with a significant amount of V(acac)₃ being formed via a chemical reaction only after addition of free ligand.¹⁰ Such processes may be represented by reactions 4 and 5 in Table I.

V(acac)₃ has been studied independently, and a typical voltammogram shows distinct couples at -1.42 and +0.76 V. (The voltammogram is virtually identical, except for the potentials, with that for tris(8-quinolinolato)vanadium(III), presented in Figure 1a of a previous paper.²) On the basis of the cathodic/anodic peak current ratio and the peak potential separation, the couple at -1.42 V is reversible. Coulometric data also indicate that it is a one-electron process, and the voltammogram obtained after the reduction process indicates

(9) Neal, T. E.; Murray, R. W. *Anal. Chem.* **1970**, *42*, 1654.
 (10) UV-visible spectra of the black solution verify the presence of traces of V(acac)₃ and even V(acac)₃⁻ under prolonged reduction times. No characteristic absorbance peaks of the V^{III} intermediate have been identified. Yet the black color is probably indicative of a mixture, and it is only after addition of ligand that the solution turns distinctly yellow and exhibits the spectrum of V(acac)₃ (Figure 7) with absorbances indicative of a 1 mM solution.

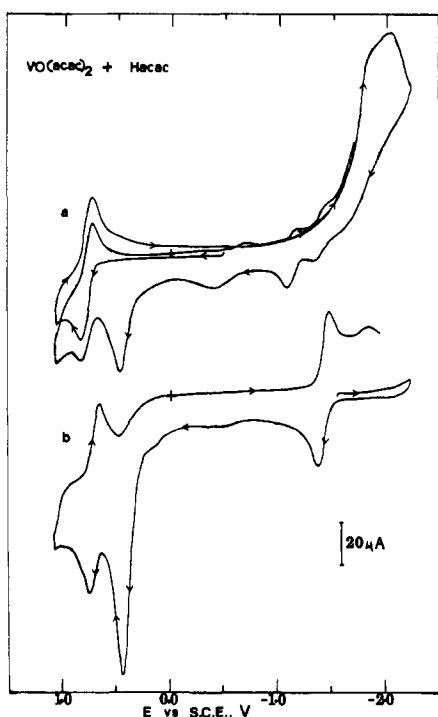


Figure 3. Cyclic voltammograms in 0.1 M TEAP/Me₂SO solution of (a) 1 mM VO(acac)₂ plus 6 mM Hacac and (b) solution a after reduction at -2.1 V (scan rate 0.2 V/s).

that the initial product is stable. Reoxidation produces V(acac)₃ quantitatively.

A 1 mM solution of VO(acac)₂ with sixfold excess ligand was studied to simulate Kitamura's conditions. The voltammogram in Figure 3a shows a ligand reduction peak overlapping those for vanadium reduction; otherwise the data agree with Kitamura's polarogram. Note that under these conditions no oxidation peak is present at +0.25 V. (So that solvent effects could be checked, a voltammogram was recorded for a similar solution in acetonitrile. No significant difference were observed. Likewise, for the reduction of VO(acac)₂ without free ligand present, the same products are observed in acetonitrile as in Me₂SO.)

Reduction of this solution at -2.1 V produces a green solution which slowly changes to dark blue as the electrolysis proceeds. The number of coulombs consumed is very high, being more than three times the value expected for a two-electron process. The cyclic voltammogram of the intermediate green solution indicates that it contains V(acac)₃. The dark blue solution of the final product contains V(acac)₃⁻ which was verified by comparing Figure 3b with the voltammogram of V(acac)₃ obtained after reduction by one electron. The dark blue color also matches that of V(acac)₃⁻ produced chemically by Schaeffer.¹¹ Figure 3b also shows that the excess ligand has been reduced which explains why such a high coulometric value was obtained.

These results indicate (in agreement with Kitamura) that in the presence of excess free ligand VO(acac)₂ is reduced by two electrons to V(acac)₃⁻. In contrast to Kitamura's work, our work demonstrates that ligand addition is a separate step occurring after the first one-electron reduction. Since VO(acac)₂ is reduced at -1.90 V and V(acac)₃ at a more positive potential (-1.42 V), V(acac)₃ produced during the VO(acac)₂ reduction experiment is necessarily further reduced to V(acac)₃⁻. Furthermore, the identities of V(acac)₃ and V(acac)₃⁻ have been verified, and the proposed reactions are summarized in Table I.

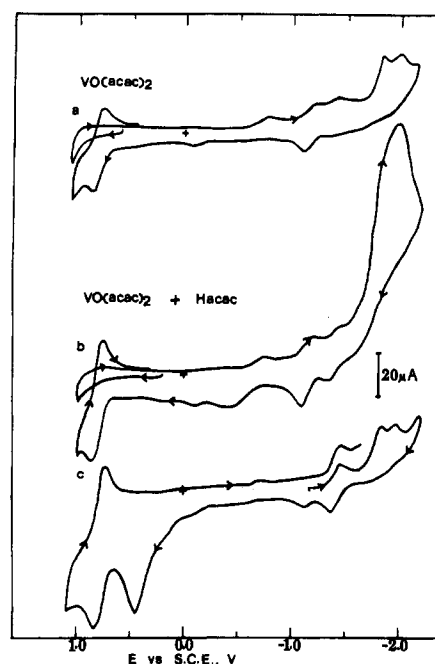


Figure 4. Cyclic voltammograms in 0.1 M TEAP/Me₂SO solution of (a) 1 mM VO(acac)₂ after oxidation at +0.95 V, (b) 1 mM VO(acac)₂ plus 6 mM Hacac after oxidation at +0.95 V, and (c) solution b after reduction at -1.55 V (scan rate 0.2 V/s).

Oxidation Processes. No oxidation processes were studied by Kitamura since the accessible positive potential range is quite limited when working with a mercury electrode. The present study was conducted with a platinum electrode, and the oxidation processes of VO(acac)₂ and V(acac)₃ are reported.

The voltammogram resulting from an initial positive scan of a 1 mM VO(acac)₂ solution exhibits a distinct couple at +0.81 V as shown in Figure 1a. On the basis of peak ratio data, the couple appears reversible although the peak potential separation of 90 mV is larger than the theoretical value. Controlled-potential coulometry at +0.95 V indicates that the process involves a one-electron oxidation, but the resulting voltammogram (Figure 4a) indicates that the initial product is unstable. Reduction peaks appear at -0.72, -1.20, and -1.45 V as well as the peaks at -1.85 and -1.95 V for VO(acac)₂.

The -1.45-V peak is near to that for V(acac)₃ reduction but does not have the same peak shape. The appearance of the VO(acac)₂ reduction peaks and the +0.81-V couple on the second scan indicates that the final V^V species can be reduced back to VO(acac)₂. The -1.20-V peak is tentatively assigned to this process. The oxidation peak at -1.1 V is not coupled to it, and the -0.72-V reduction peak has not been identified.

The tentative assignment of the -1.20-V peak is supported by reduction of this solution (Figure 4a) at -1.55 V. The resulting voltammogram is identical with that for the initial VO(acac)₂ solution.

That reduction of the overlapping peaks near -1.20 V produces VO(acac)₂ is further substantiated by the UV-vis spectra of these solutions. Spectra of the initial VO(acac)₂ solution, the solution following oxidation at +0.95 V, and the final solution resulting from a subsequent reduction at -1.55 V are shown in Figure 5. Although the visible spectra are similar, the UV spectra are distinctive. Both the initial and final solutions exhibit an absorbance peak at 320 nm and a shoulder at 270 nm, while the relative absorbances at these wavelengths are reversed for the oxidized product. On the basis of these data, reactions 1-3 in Table II are proposed.

An initial positive scan of a V(acac)₃ solution exhibits a distinct reversible couple at +0.76 V. Controlled-potential

(11) Schaeffer, W. P. *Inorg. Chem.* 1965, 4, 642.

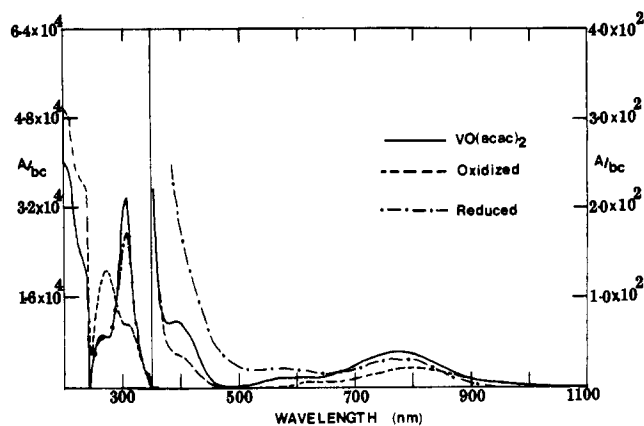


Figure 5. Absorption spectra in Me₂SO of VO(acac)₂, the product resulting from oxidation of VO(acac)₂ at +0.95 V, and the product resulting from subsequent reduction at -1.55 V of the oxidation product.

Table II. Reactions Based on the Oxidations of VO(acac)₂ and V(acac)₃

reaction	potential, V vs. SCE	
	<i>E'</i>	<i>E</i> _{pc}
(1) VO(acac) ₂ ⇌ VO(acac) ₂ ⁺ + e ⁻	+0.81	
(2) VO(acac) ₂ + <u>rapid</u> → V ^V		
(3) V ^V + e ⁻ → VO(acac) ₂		-1.20
(4) V(acac) ₃ ⇌ V(acac) ₃ ⁺ + e ⁻	+0.76	
(5) V(acac) ₃ ⁺ + H ₂ O → VO(acac) ₂ + Hacac + H ⁺		
(6) H ⁺ + e ⁻ ⇌ 1/2 H ₂		-0.55

coulometry at +0.95 V gives a value of 1.89 e/molecule suggesting oxidation to V^V. Furthermore, the resulting cyclic voltammogram (Figure 6a) shows several similarities to that for the oxidation product of VO(acac)₂ (Figure 4a). The initial product of each oxidation process is unstable, and reduction peaks appear at -1.20 and -1.45 V in both cases. The voltammogram resulting from V(acac)₃ oxidation shows free ligand and a reduction peak at -0.55 V which are not present in the solution derived from VO(acac)₂.

The reduction peak at -1.20 V suggests that the same V^V species is produced from both starting materials. The similarity of the UV spectra of oxidized VO(acac)₂ and oxidized V(acac)₃ (Figure 7) substantiates this. The free ligand peak produced by oxidation of V(acac)₃ implies dissociation of at least 1 ligand/molecule. Addition of perchloric acid to the V(acac)₃ product increases the height of the peak at -0.55 V while addition of tetraethylammonium hydroxide eliminates it. Furthermore, a voltammogram of perchloric acid produces a similar peak, suggesting that the process involves the reduction of protons.

On the basis of these data, a mechanism for V(acac)₃ oxidation is proposed (reactions 4-6, Table II). The initial product of V(acac)₃ oxidation is V(acac)₃⁺. This cation reacts rapidly with residual water in the solvent to produce VO(acac)₂, free ligand, and protons. During electrolysis at +0.95 V, the VO(acac)₂ produced is subsequently oxidized to V^V.

Reduction of the V^V solution originating from V(acac)₃ is more complicated than the corresponding process when VO(acac)₂ is the initial species. Reduction at -1.55 V of V^V (from V(acac)₃) is a three-electron process overall (coulometric data 2.60 e/molecule).

An intermediate is observed by stopping the electrolysis before completion. A corresponding voltammogram is shown in Figure 6b. The couple at -1.42 V indicates that V(acac)₃ is the dominant species at this stage. Upon completion of the electrolysis, the oxidation wave of this couple is present on the

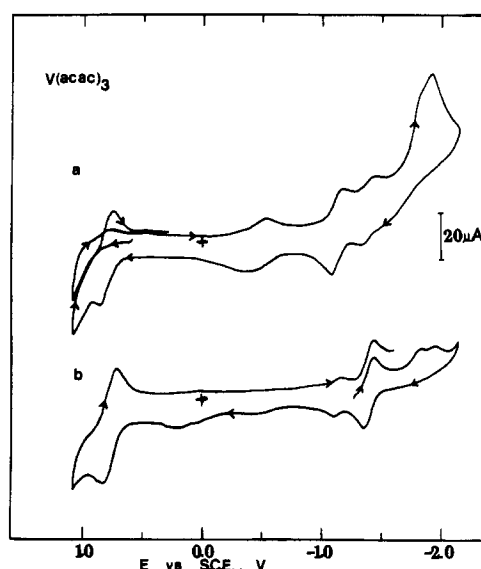


Figure 6. Cyclic voltammograms in 0.1 M TEAP/Me₂SO solution of (a) 1 mM V(acac)₃ after oxidation at +0.95 V and (b) solution a after reduction at -1.55 V (scan rate 0.2 V/s).

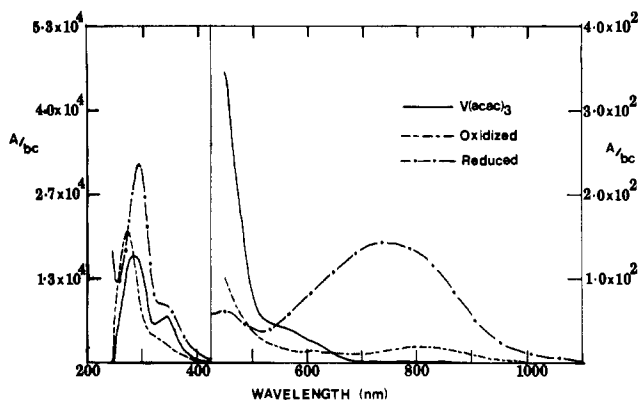


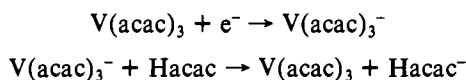
Figure 7. Absorption spectra in Me₂SO of V(acac)₃, the product resulting from oxidation of V(acac)₃ at +0.95 V, and the product resulting from reduction of V(acac)₃ at -1.55 V.

initial scan. The spectrum of the final solution shows a large absorbance at 740 nm just as is observed for the one-electron reduction product of V(acac)₃ (Figure 7). Thus, the overall process appears to be V^V + 3e⁻ → V(acac)₃⁻.

These results imply that the three-electron reduction of V^V occurs only in the presence of excess ligand. So that this could be verified, the above oxidation and reduction series was carried out on a solution of 1 mM VO(acac)₂ and 6 mM Hacac. The voltammogram resulting from the oxidation step is shown in Figure 4b. This cyclic voltammogram is identical with that for oxidized V(acac)₃ except for the size of the ligand peak. Subsequent reduction at -1.55 V produces V(acac)₃ as an intermediate (Figure 4c) and finally V(acac)₃⁻.

The reduction of V^V to V^{II} appears to incorporate the two-electron reduction of VO(acac)₂ discussed earlier (reactions 1, 2, 4, and 5, Table I), but two inconsistencies appear. First, although VO(acac)₂ is produced during electrolysis at -1.55 V, this potential is not negative enough to reduce VO(acac)₂ further. Second, Figure 4c indicates that free ligand is also reduced by this process, although its reduction potential is -2.06 V.

A possible explanation of the ligand reduction comes from Kitamura's work.⁶ He observed that V^{II} has a catalytic effect on ligand reduction. His proposal includes the following cyclic process which involves ligand reduction at a potential less negative than in the absence of vanadium.



The final products are $\text{V}(\text{acac})_3^-$ and reduced ligand, as observed in our work.

The apparent reduction of $\text{VO}(\text{acac})_2$ at -1.55 V cannot be explained from the present data. The complexity of the $\text{V}^{\text{V}} + e^- \rightarrow \text{VO}(\text{acac})_2$ process. Thus, current work involves attempts to synthesize and study several V^{V} species directly. New data from these studies should help clarify the nature of the V^{V} species and its reactions.

Conclusions

A comparison of the oxidation-reduction behavior of analogous vanadium(III) compounds in aprotic solvents shows a distinct similarity. $\text{V}(\text{acac})_3$, VQ_3 ($\text{Q}^- = 8$ hydroxyquinoline anion), and $\text{V}(\text{dtc})_3$ ($\text{dtc}^- =$ diethyldithiocarbamate anion) each exhibit reversible one-electron reductions between -1.0 and -1.5 V. These compounds also show oxidations between $+0.25$ and $+1.0$ V. The oxidations of $\text{V}(\text{acac})_3$ and VQ_3 are

reversible only on the cyclic voltammetry time frame, while the reversibility of $\text{V}(\text{dtc})_3$ depends on concentration. Only $\text{V}(\text{acac})_3$ undergoes a further oxidation to vanadium(V).

The vanadium(IV) species show few similarities to one another. Although $\text{VO}(\text{dtc})_2$ and $\text{VO}(\text{acac})_2$ are irreversibly reduced, no distinct reduction wave for VOQ_2 is observed. Only $\text{VO}(\text{acac})_2$ shows a reversible oxidation ($+0.81$ V). VOQ_2 is oxidized at a similar potential ($+0.775$ V), but the process is irreversible. No oxidation of $\text{VO}(\text{dtc})_2$ is observed.

It is clear that the type of bonding atoms and the ring size (metal to bidentate ligand) are not of great significance for $\text{V}^{\text{III}}\text{L}_3$ ($\text{L} =$ bidentate ligand) compounds. In contrast, these factors appear to strongly influence the electrochemistry of $\text{V}^{\text{IV}}\text{OL}_2$ complexes. Comparisons of V^{V} complexes should be possible with data from our next study.

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Registry No. $\text{V}(\text{acac})_3$, 13476-99-8; $\text{VO}(\text{acac})_2$, 3153-26-2.

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Conformational Equilibria in Pyridine Adducts of Fluorinated Metal Acetylacetonates

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We have used NMR spectroscopy to study $\text{Ni}(\text{HFAA})_2$ and $\text{Co}(\text{HFAA})_2$ ($\text{HFAA} =$ hexafluoroacetylacetonate) in the presence of varying pyridine concentrations over a range of temperatures. Complexes with both 1 mol (1:1 complexes) and 2 mol (1:2 complexes) of pyridine coordinated to the metal atom were observed. In the case of the cobalt complex both cis and trans isomers of the 1:1 and 1:2 complexes were detected. At room temperatures the various isomers are in rapid equilibrium, and the ^{19}F NMR lines are exchange averaged. At lower temperatures the rate of exchange is slowed, and well-resolved NMR spectra are observed from all of the possible isomers. In acetone solutions the cis isomer is favored over the trans isomer in both the 1:1 and 1:2 complexes. The NMR shift of the signal from the nickel complex is mainly due to the Fermi contact interaction while the shifts of lines from the various cobalt complexes are due to both the electron-fluorine dipolar interaction and the Fermi contact interaction.

Introduction

The isotropic NMR shifts observed from cobalt complexes in solution may receive contributions from both Fermi contact and dipolar interactions.¹ The dipolar shifts arise because of anisotropy in the magnetic susceptibility which is not averaged by molecular reorientation. The equations describing the Fermi contact ($\Delta\nu/\nu_0$)_F and dipolar ($\Delta\nu/\nu_0$)_D contributions to the total isotropic shift may be written as eq 1. In this

$$(\Delta\nu/\nu_0)_F = -A \left(\frac{\gamma_e}{\gamma_N} \right) \frac{g\beta S(S+1)}{3kT}$$

$$(\Delta\nu/\nu_0)_D = -\frac{1}{3N} \left[\chi_x - \frac{\chi_x}{2} - \frac{\chi_y}{2} \right] G(\theta, r) - \frac{1}{2N} [\chi_x - \chi_y] G'(\theta, \Omega, r)$$

$$G(\theta, r) = \langle (3 \cos^2 \theta - 1)/r^3 \rangle_{\text{av}}$$

$$G'(\theta, \Omega, r) = \langle (\sin^2 \theta \cos 2\Omega)/r^3 \rangle_{\text{av}} \quad (1)$$

expression A is the Fermi contact coupling constant, the χ 's are the principal components of the magnetic susceptibility,

and r is the electron-nucleus separation, while θ and Ω determine the angles between the electron-nucleus vector and the components of the susceptibility. The dipolar term is seen to depend on the magnitude of the magnetic anisotropy, the separation of the nucleus from the metal, and the relative geometry of a given nucleus with respect to the magnetic axes. The Fermi contact term depends on the mechanism for spin delocalization from the metal into a given ligand and the spin distribution in the ligand. Octahedral cobalt(II) complexes have a T_1 ground state which is split into A and E states in the presence of tetragonal distortion. The A state is the ground state and is separated from the E state by the tetragonal distortion energy. In the case of 1:1 complexes of $\text{Co}(\text{HFFA})_2$ with pyridine one predicts a tetragonally distorted complex with changes in the components of the magnetic susceptibility. The various cis and trans isomers which are possible may also have different symmetries with different values for the components of the susceptibilities. These changes in symmetries and susceptibilities will produce variations in the dipolar shifts.

Proton and ^{13}C NMR have been used to investigate a number of base adducts of acetylacetonate (AA) complexes. Happe and Ward² studied pyridine adducts of cobalt(II) and nickel(II) AA complexes and attempted to separate the relative

(1) G. N. LaMar, W. D. Horrocks, and R. H. Holm, Eds., "NMR of Paramagnetic Molecules", Academic Press, New York, 1973.

(2) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).