

## Electrochemical Studies of Vanadium(V) Acetylacetonate Complexes in Dimethyl Sulfoxide

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Received June 9, 1981

The electrochemistry of  $\text{VO}_2(\text{acac})(\text{phen})$  and  $\text{V}_2\text{O}_4(\text{acac})_2$  ( $\text{acac}^-$  = acetylacetonate anion, phen = 1,10-phenanthroline) has been studied by cyclic voltammetry and controlled-potential coulometry in dimethyl sulfoxide at a platinum electrode.  $\text{VO}_2(\text{acac})(\text{phen})$  is reduced at  $-1.45$  V vs. SCE, and  $\text{V}_2\text{O}_4(\text{acac})_2$  is reduced at  $-1.30$  V, both by 1 electron/mol of vanadium processes. The major product in both cases is  $\text{VO}(\text{acac})_2$ . If excess ligand is present, these reduction processes require three electrons and give  $\text{V}(\text{acac})_3^-$  as the final product. The electrochemical and spectroscopic data indicate that  $\text{VO}_2(\text{acac})$ ,  $\text{V}_2\text{O}_4(\text{acac})_2$ , and a third species, tentatively identified as  $\text{VO}(\text{OH})_2(\text{acac})$ , exist in equilibrium with one another and are the predominant products of the oxidation of  $\text{VO}(\text{acac})_2$  and  $\text{V}(\text{acac})_3^-$ .  $\text{VO}(\text{OH})_2(\text{acac})$  is reduced to  $\text{VO}(\text{acac})_2$  at  $-1.20$  V. The equilibria are acid-base controlled, and the two monomeric vanadium(V) species are dominant in dimethyl sulfoxide.

### Introduction

We have reported recently<sup>1</sup> on the electrochemistry of  $\text{VO}(\text{acac})_2$  and  $\text{V}(\text{acac})_3^-$  ( $\text{acac}^-$  = acetylacetonate anion) and clarified the reduction pathway for  $\text{VO}(\text{acac})_2$  suggested by Kitamura and co-workers.<sup>2-4</sup> We also examined the oxidation processes of these compounds, which had not been explored previously. Although the cyclic voltammograms indicated reversible oxidation processes for both of these species, more complex solutions resulted from bulk controlled-potential electrolysis. In fact, based on the resulting cyclic voltammograms, the one-electron oxidation of  $\text{VO}(\text{acac})_2$  and the two-electron oxidation of  $\text{V}(\text{acac})_3^-$  were found to give the same final vanadium(V) products. We wish to report here on electrochemical studies of several vanadium(V) complexes which are the major products of those oxidation processes.

### 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.

Experiments were carried out in a Vacuum Atmospheres Co. Model HE-43-2 glovebox with an HE 493 Dri-train, under a dry-nitrogen atmosphere. A simple electrochemical cell open to the box atmosphere was used.

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

**Reagents.** High-purity dimethyl sulfoxide (0.018% water) and acetonitrile (0.003% water) were obtained from Burdick and Jackson Laboratories and used as received. Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium bromide (Aldrich) and perchloric acid as described previously<sup>5</sup> and was used as the supporting electrolyte. Tetraethylammonium hydroxide was obtained from Aldrich as a 25% solution in water.

**Dioxo(2,4-pentanedionato)(1,10-phenanthroline)vanadium(V).**  $\text{VO}_2(\text{acac})(\text{phen})$  was prepared by the method of Taguchi et al.<sup>6</sup> Excess 1,10-phenanthroline in dichloromethane was added to a solution of  $\text{VO}(\text{acac})_2$  (1.0 g, 0.0038 mol) (Alfa) in the same solvent. The mixture was oxidized by bubbling with oxygen gas and yielded reddish brown crystals. The product was collected, washed with diethyl ether, and recrystallized from a mixture of methanol and acetylacetone. Anal. Calcd: C, 56.36; H, 4.17. Found: C, 55.78; H, 4.03.

**$\mu$ -Dioxo-bis(oxo(2,4-pentanedionato)vanadium(V)).**  $\text{V}_2\text{O}_4(\text{acac})_2$  was prepared by one of several methods given by Doadrio and Carro.<sup>7</sup> Approximately 7.8 g of  $\text{NaVO}_3 \cdot 4\text{H}_2\text{O}$  (0.04 mol) was dissolved in 80 mL of water. To this solution was added 4.0 g (0.04 mol) of acetylacetone with warming to complete dissolution. After the solution was cooled, HCl was added dropwise to adjust the pH to 1.5. A crystalline product was then obtained only after chilling in a refrigerator for 24 h. The product was washed with water and acetone and vacuum-dried over  $\text{P}_2\text{O}_5$ . Anal. Calcd: C, 32.81; H, 4.40. Found: C, 32.04; H, 4.12.

### Results and Discussion

The vanadium(V) products resulting from the oxidation of  $\text{VO}(\text{acac})_2$  or  $\text{V}(\text{acac})_3^-$  cannot easily be isolated since they are present at low concentrations (less than 1 mM) while the supporting electrolyte is present at much higher concentration (0.1 M TEAP). Thus, qualitative identification has been attempted by comparing the cyclic voltammograms of several vanadium(V) complexes to those of the oxidation products. The electrochemically produced species exhibit reductions at  $-1.20$  and  $-1.45$  V vs. SCE. Although several species showed no reductions in this region,<sup>8</sup>  $\text{VO}_2(\text{acac})(\text{phen})$  and  $\text{V}_2\text{O}_4(\text{acac})_2$  showed similar reduction peaks.

An initially cathodic cyclic voltammogram of 1 mM  $\text{VO}_2(\text{acac})(\text{phen})$  is shown in Figure 1a. The major reduction peak at  $-1.45$  V vs. SCE has a small prewave at  $-1.20$  V, and the peak at  $-2.1$  V appears to be part of a reversible couple. Figure 1b is a voltammogram of 1,10-phenanthroline and exhibits a distinct reversible couple at  $-2.1$  V, similar to that present in Figure 1a. The reduction at  $-2.1$  V can, therefore, be assigned to the 1,10-phenanthroline ligand, and its position is apparently not affected by the metal. Thus, in the solution of the complex, the 1,10-phenanthroline ligand may be completely dissociated.

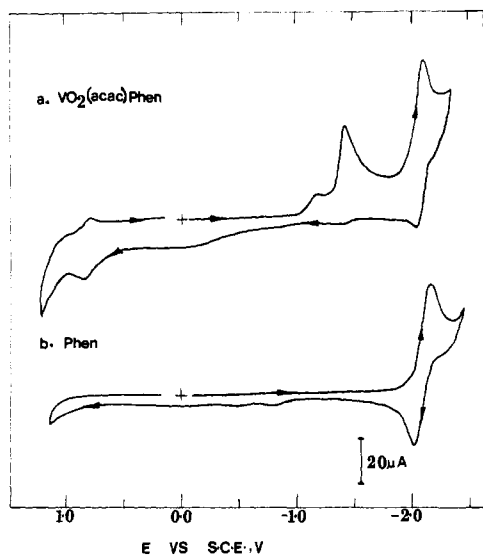
The peak at  $-1.45$  V may be assigned to the reduction of  $\text{VO}_2(\text{acac})(\text{phen})$  or the dissociated species,  $\text{VO}_2(\text{acac})$ . A

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(8) The compounds  $\text{VO}(\text{acac})_2\text{Cl}$  and  $\text{VO}(\text{acac})\text{Cl}_2$  were synthesized by the method of Funk (Funk, H.; Weiss, W.; Zeising, M. *Z. Anorg. Allg. Chem.* **1958**, *296*, 361) but showed no significant reduction peaks. Although  $\text{VO}(\text{acac})_3$  has been reported in the literature as a catalyst for organic reactions, attempts to synthesize this compound were unsuccessful. The compound  $\text{VO}_2(\text{acac})\text{phen}$  was investigated as a source for the vanadium(V) moiety,  $\text{VO}_2^+$ .



**Figure 1.** Cyclic voltammograms in 0.1 M TEAP-Me<sub>2</sub>SO solution of (a) 1 mM VO<sub>2</sub>(acac)(phen) and (b) 1 mM 1,10-phenanthroline. Scan rate = 0.2 V/s.

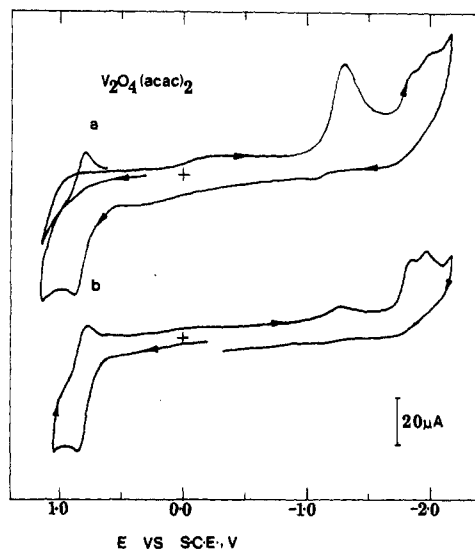
similar cyclic voltammogram recorded in acetonitrile shows a much smaller prewave at -1.20 V. Since the residual water content of the acetonitrile is much lower than that of the Me<sub>2</sub>SO (0.003% vs. 0.018%), a hydrolysis product is likely. Such a species, formulated as VO<sub>3</sub>H<sub>2</sub>(acac), has been proposed by Doadrio and Carro.<sup>7</sup> Further data to be presented below suggest that the species reduced at -1.2 V may actually be VO(OH)<sub>2</sub>(acac).

An initially anodic scan of VO<sub>2</sub>(acac)(phen) shows no oxidations, yet after a cathodic scan has been carried to a potential more negative than -1.45 V, the couple at +0.81 V appears. This couple corresponds to VO(acac)<sub>2</sub>. Following controlled-potential electrolysis at -1.60 V (a one-electron process), the voltammogram is similar to that of VO(acac)<sub>2</sub><sup>9</sup> with the 1,10-phenanthroline couple superimposed. Of major importance is that the couple at +0.81 V is now present on an initially anodic scan.

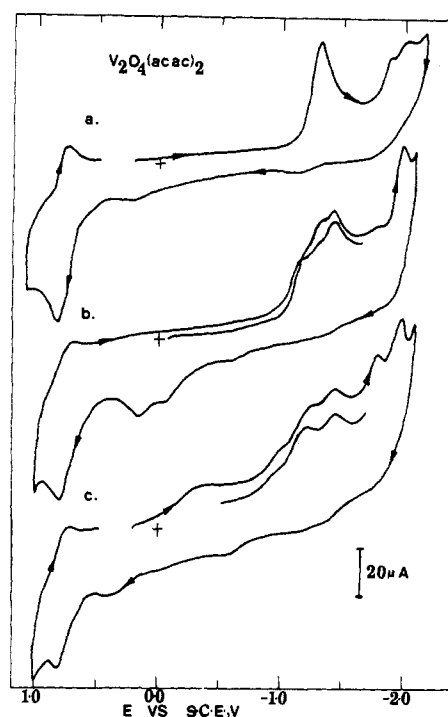
Figure 2a is a cyclic voltammogram of the dimeric vanadium(V) complex, V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub>. The major reduction peak at -1.30 V can be assigned to reduction of the dimer, while the smaller peaks at -1.85 and -1.95 V represent free ligand and VO(acac)<sub>2</sub>. Although no oxidation peaks are present on an initially anodic scan, the couple at +0.81 V appears on a second scan. As for the reduction of VO<sub>2</sub>(acac)(phen), the controlled-potential electrolysis of V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub> at -1.60 V consumes 1 electron/mol of vanadium. In this case, the voltammogram of the resulting solution (Figure 2b) is virtually identical with that for VO(acac)<sub>2</sub>.<sup>9</sup>

The cyclic voltammograms of VO<sub>2</sub>(acac)(phen) and V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub> indicate that these species have reduction potentials similar to those of the oxidation products of VO(acac)<sub>2</sub>, and in fact both can be reduced to VO(acac)<sub>2</sub>. In order to identify pathways by which these vanadium(V) species might be formed, we considered the results of Doadrio and Carro.<sup>7</sup> These workers synthesized the dimer, V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub>, but found that it hydrolyzed in water to give monomeric species. The equilibria between forms was shown to be pH controlled. Thus, we have carried out experiments varying the acid and base content of our solutions to observe possible shifts in equilibria.

Figure 3a shows that a solution of pure V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub> has only a single distinct reduction peak at -1.30 V in the region of interest. As shown in Figure 3b, addition of approximately



**Figure 2.** Cyclic voltammograms in 0.1 M TEAP-Me<sub>2</sub>SO solution of (a) 1 mM V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub> and (b) solution a after reduction at -1.60 V. Scan rate = 0.2 V/s.



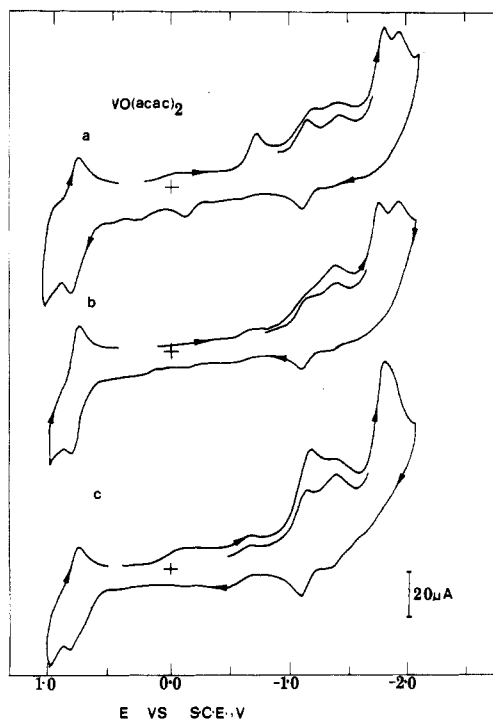
**Figure 3.** Cyclic voltammograms in 0.1 M TEAP-Me<sub>2</sub>SO solution of (a) 1 mM V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub>, (b) solution a after addition of 1 equiv of TEAOH and a trace of 1,10-phenanthroline, and (c) solution b after addition of excess HClO<sub>4</sub>. Scan rate = 0.2 V/s.

1 equiv of base (TEAOH) to this solution produces peaks at -1.30 and -1.45 V.<sup>10</sup> The second consecutive scan indicates a further process giving rise to a third peak at -1.20 V. Thus, under basic conditions the peak at -1.45 V is dominant, while the -1.30-V peak is least important.

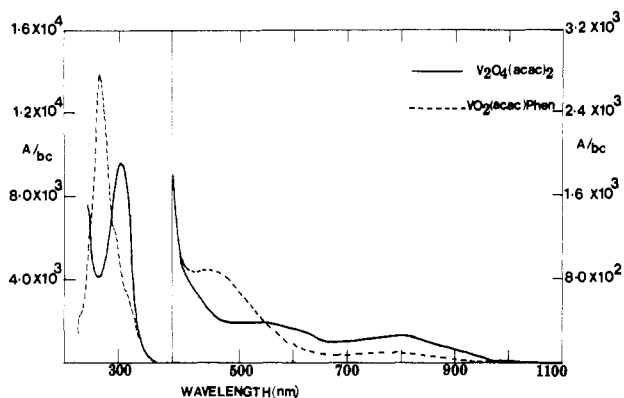
When excess acid (HClO<sub>4</sub>) (Figure 3c) is added to this solution, the peak at -1.30 V disappears and the peak at -1.20 V becomes more dominant. The second scan (shown below the complete cycle) suggests that the species reduced at -1.20 V is present in higher concentration than that reduced at -1.45 V.

(9) See Figure 1a in ref 1.

(10) A trace of 1,10-phenanthroline was added as it was found to sharpen the peaks. This probably aids in complexation by filling coordination positions otherwise filled by Me<sub>2</sub>SO.



**Figure 4.** Cyclic voltammograms in 0.1 M TEAP–Me<sub>2</sub>SO solution of (a) 1 mM VO(acac)<sub>2</sub> after oxidation at +0.95 V, (b) solution after addition of 1 equiv of TEOH and a trace of 1,10-phenanthroline, and (c) solution after addition of excess HClO<sub>4</sub>. Scan rate = 0.2 V/s.



**Figure 5.** Absorption spectra in Me<sub>2</sub>SO of V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub> and VO<sub>2</sub>(acac)(phen).

A similar experiment was carried out with VO<sub>2</sub>(acac)(phen). Although the reduction peaks are less distinct, the same peaks appear dominant under similar conditions.

This experiment was also performed on the oxidation products of VO(acac)<sub>2</sub>. The initial voltammogram of oxidized VO(acac)<sub>2</sub> is shown in Figure 4a and exhibits reduction peaks at –1.20 and –1.45 V of similar size. The initial scan following addition of base (Figure 4b) shows an enhancement of the –1.45-V reduction peak. In contrast, the addition of acid (Figure 4c) shows a dramatic enhancement of the –1.20-V reduction process. In each case the partial cycle shown below the complete voltammogram indicates further shifts in the equilibria. Note that in no case is the –1.30-V reduction process dominant.

These data suggest that three species are present in equilibrium. UV–visible spectra have been recorded to help verify the actual species present. The electronic spectra of solutions of VO<sub>2</sub>(acac)(phen) and V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub> in Me<sub>2</sub>SO are shown in Figure 5. Both spectra show a slight absorbance at 800 nm which is similar to the spectra of the vanadium(V) species

**Table I.** Reactions of Vanadium(V) Acetylacetonate Complexes

eq no.	reaction	$E_{pc}$ , V vs. SCE
1	$V_2O_4(acac)_2 + 2e^- \rightarrow V_2O_4(acac)_2^{2-}$	–1.30
2	$V_2O_4(acac)_2^{2-} + 2H_2O \rightarrow VO(acac)_2 + VO^{2+} + 4OH^-$	
3	$VO_2(acac)(phen) + e^- \rightarrow VO_2(acac)(phen)^-$	–1.45
4	$2VO_2(acac)(phen)^- + 2H_2O \rightarrow VO(acac)_2 + VO^{2+} + 4OH^- + 2phen$	
5	$2VO(acac)_2^+ + 2H_2O \rightarrow V_2O_4(acac)_2 + 2Hacac + 2H^+$	
6	$V_2O_4(acac)_2 = 2VO_2(acac)$	
7	$VO_2(acac) + H_2O \xrightleftharpoons[base]{acid} VO(OH)_2(acac)$	
8	$VO_2(acac)(phen) + H_2O \rightarrow VO(OH)_2(acac) + phen$	
9	$VO(OH)_2(acac) + e^- \rightarrow VO(OH)_2(acac)^-$	–1.20
10	$2VO(OH)_2(acac)^- \rightarrow VO(acac)_2 + VO^{2+} + 4OH^-$	

generated from VO(acac)<sub>2</sub> and V(acac)<sub>3</sub>.<sup>1</sup> These spectra are also similar in the UV region to the electrochemically generated species, but other minor products may also have been produced during the electrochemical step. (Also, the sharp absorbance peak at 260 nm in the spectrum of VO<sub>2</sub>(acac)(phen) is due to 1,10-phenanthroline.) The spectra of the reduction products of VO<sub>2</sub>(acac)(phen) and V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub> are virtually identical with the spectrum of VO(acac)<sub>2</sub>. Spectra were also recorded for solutions of VO<sub>2</sub>(acac)(phen), V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub>, and oxidized VO(acac)<sub>2</sub> following additions of acid and base. As expected, these spectra indicate the presence of mixtures in each case.

Our earlier work also showed that in the presence of free ligand the electrochemically generated vanadium(V) species were reduced by 3 electrons to give V(acac)<sub>3</sub><sup>–</sup>. A similar experiment has been carried out with V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub>. When this species is reduced at –1.60 V in the presence of free ligand, the resulting cyclic voltammogram exhibits an oxidation peak at –1.40 V. This peak corresponds to V(acac)<sub>3</sub><sup>–</sup> and is the reversible reduction product of V(acac)<sub>3</sub>.<sup>1</sup> The voltammogram is identical with that for reduction of the electrochemically generated vanadium(V) species with free ligand present.

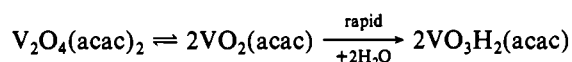
Proposed reactions for the vanadium(V) acetylacetonate complexes are presented in Table I. The dimeric species, V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub>, is reduced by 1 electron/mol of vanadium at –1.30 V (reaction 1). The cyclic voltammograms indicate that the initial product is not stable but rather VO(acac)<sub>2</sub> results. The ligand/metal stoichiometry of this complex requires that a “free” vanadium species must also be formed. Reaction 2 suggests that a hydrolysis reaction fits this data. The vanadyl ion could be coordinated by hydroxide ion or Me<sub>2</sub>SO, but no acetylacetonate ligands are available.

The mixed-ligand complex, VO<sub>2</sub>(acac)(phen), is reduced by 1 electron at –1.45 V (reaction 3). Reaction 4 is analogous to reaction 2 and is proposed since the final product in both cases is VO(acac)<sub>2</sub>. It is not clear at what point the 1,10-phenanthroline ligand dissociates, but it does not appear to affect the electrochemistry of the vanadium complexes. Its effect of sharpening the reduction peaks on some of the cyclic voltammograms may indicate that it serves to complete the coordination spheres of some complexes or acts as a mediator by being adsorbed on the platinum electrode.

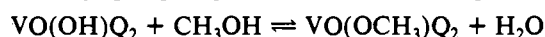
As reported earlier,<sup>1</sup> on the time scale of cyclic voltammetry, VO(acac)<sub>2</sub> is reversibly oxidized to VO(acac)<sub>2</sub><sup>+</sup> at +0.81 V. Following controlled-potential electrolysis of the bulk solution, the resulting cyclic voltammogram no longer indicates the presence of VO(acac)<sub>2</sub><sup>+</sup>. It is clear that during the time required for electrolysis, the initial product has reacted further. These results in Me<sub>2</sub>SO lead to the reduction peaks at –1.20 and –1.45 V. When a similar experiment is carried out in acetonitrile, the initial product is stable, with the reversible couple at +0.81 V persisting. Since the residual water content of Me<sub>2</sub>SO is significantly higher, this suggests a hydrolysis

reaction in this solvent. We propose that the dimer, V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub>, is formed via reaction 5 as an intermediate and is one of the three important vanadium(V) species produced in Me<sub>2</sub>SO.

The other important species are VO<sub>2</sub>(acac) and VO(OH)<sub>2</sub>(acac) and are in equilibrium with the dimer (reactions 6 and 7). Our data and that of Doadrio and Carro<sup>7</sup> are consistent with these propositions. These workers concluded that the dimer dissociates to a monomer which rapidly hydrolyzes in water:



The hydrolyzed species could not be isolated but showed behavior similar to VO(OH)(OCH<sub>3</sub>)(acac), which was isolated. The presence of a hydroxyl group in this compound was verified by its IR spectrum. Also, a solution of V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub> gives a red color when mixed with alcohols. This is a well-known qualitative test for alcohols<sup>11</sup> and involves the conversion of a hydroxyl group to give an ester. For example:



(Q = 8-hydroxyquinoline anion).<sup>12</sup> This implies that the dimer reacts to form an intermediate with a hydroxyl group before forming an ester.

In nonaqueous solvents the monomer, VO<sub>2</sub>(acac), would be expected to be more stable, as observed in our work and given by reaction 6. Nonetheless, the hydrolysis reaction is also important, as indicated by the comparison of the results in Me<sub>2</sub>SO and acetonitrile. This suggests the formation of VO(OH)<sub>2</sub>(acac) by reaction 7. This is the species formulated by Doadrio and Carro as VO<sub>3</sub>H<sub>2</sub>(acac), but the similarity to VO(OH)(OCH<sub>3</sub>)(acac) suggests two hydroxyl ligands.

In our system the equilibrium (reaction 7) is shifted toward VO(OH)<sub>2</sub>(acac) by acid and toward VO<sub>2</sub>(acac) by base. The dimer, V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub>, is dominant only in an initial solution prepared from that compound.

The cyclic voltammogram of VO<sub>2</sub>(acac)(phen) indicates that predissociation of the 1,10-phenanthroline ligand occurs if residual water is present in the solvent. This reaction produces the hydroxyl species (reaction 8). The reduction process at -1.20 V is assigned to this species (reaction 9). Finally, since reduction of VO(OH)<sub>2</sub>(acac) leads back to VO(acac)<sub>2</sub>,

reaction 10 is proposed. The ligand/metal stoichiometry once again indicates that a free vanadyl ion is formed (as in reactions 2 and 4).

One consequence of the proposed mechanism is that all of the vanadium(V) complexes exhibit 1/1 stoichiometry of acetylacetonate to metal. Thus, the oxidations of VO(acac)<sub>2</sub> and V(acac)<sub>3</sub> should give 1 and 2 equiv of free ligand, respectively. The oxidation of V(acac)<sub>3</sub> does produce free ligand, while little or no free ligand is observed in the voltammogram of the VO(acac)<sub>2</sub> oxidation product.

Further study of the reduction of VO(acac)<sub>2</sub> has clarified this point. The voltammograms of VO(acac)<sub>2</sub> exhibit two overlapping reduction peaks at -1.85 and -1.95 V.<sup>1</sup> A study in aqueous solution by Trujillo and Brito<sup>13</sup> suggests that VO(acac)<sub>2</sub> dissociates to VO(acac)<sup>+</sup> and acac<sup>-</sup>. We have monitored the gradual production of VO(acac)<sub>2</sub> in Me<sub>2</sub>SO by cyclic voltammetry. Neutral acetylacetonate was reduced, giving acac<sup>-</sup>, and then small amounts of VO(ClO<sub>4</sub>)<sub>2</sub>·5Me<sub>2</sub>SO<sup>14</sup> were added. The reduction peaks at -1.85 and -1.95 V appeared, with the first peak decreasing and the second peak increasing as further additions of vanadium were made. Thus, reduction of ligand occurs at -1.85 V, while the complex is reduced at -1.95 V, and apparently the dissociation proposed by Trujillo also occurs in Me<sub>2</sub>SO. Next, free ligand was added to VO(acac)<sub>2</sub> in small increments. The voltammograms show that a significant excess of ligand must be added before an increase in the -1.85-V peak is observed. Thus, the absence of a ligand peak following oxidation of VO(acac)<sub>2</sub> does not conflict with our proposed mechanism for the vanadium(V) complexes.

### Conclusions

A series of equilibria exist between the three vanadium(V) species, V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub>, VO<sub>2</sub>(acac), and VO(OH)<sub>2</sub>(acac). The equilibria are shifted by acid, base, and residual water in the solvents. These species are also the major products of oxidation of VO(acac)<sub>2</sub> and V(acac)<sub>3</sub>. When produced electrochemically, the two monomeric forms are dominant in Me<sub>2</sub>SO. Reduction of these species gives VO(acac)<sub>2</sub>, while reduction in the presence of excess ligand gives V(acac)<sub>3</sub><sup>-</sup>.

**Acknowledgment.** This work was supported by the Research Corp., the National Science Foundation under Grant No. CDP 8001911, and the Faculty Research Committee of Miami University.

**Registry No.** V<sub>2</sub>O<sub>4</sub>(acac)<sub>2</sub>, 81194-27-6; VO<sub>2</sub>(acac)(phen), 55410-98-5; VO(OH)<sub>2</sub>(acac), 14219-92-2; VO(acac)<sub>2</sub>, 3153-26-2.

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