structural evidence for this complex was provided, however, by the authors. Previous studies with Cr(III) and Co(III) complexes of ADP and ATP have shown that N(7) and N(1) of the heterocyclic ring does not insert into the coordination sphere of the metal ion. In order to ensure that this was also the case with RhATP and RhADP, we examined both the absorption and elliptical properties of the adenine ring present in the complexes and found that they were no different from those of the adenine ring of uncomplexed ADP and ATP. In addition, Rh(III) coordination to these nucleotides does not alter the ¹³C NMR spectral properties and therefore we feel confident that only the phosphoryl oxygens serve as ligands in these complexes.

It is interesting to note the difference in behavior of the Rh(III), Co(III), and Cr(III) ATP complexes. $Cr(NH_3)_3$-$(H_2O)ATP$ and $Cr(H_2O)_4ATP$ are stable bidentate complexes. $Cr(H_2O)_4ATP$ converts to what is believed to be the α,β,γ-tridentate complexes only under strongly acidic conditions.[7,15] $Co(NH_3)_3(H_2O)ATP$ is not stable but spontaneously converts to the α,β,γ-$Co(NH_3)_3ATP$ tridentate complex.[15] Bidentate $Rh(H_2O)_4ATP$, on the other hand, can be transformed to the tridentate complex by heating it at pH 3 or by allowing it to stand at 4 °C (pH 2–5) over a period of several days. Preliminary studies indicate that both the α,β,γ-tridentate Rh-$(H_2O)_3ATP$ and the β,γ-bidentate $Rh(H_2O)_4ATP$ stereoisomers (whose presence is apparent from the ³¹P NMR spectra of the given structural isomer) can be resolved on both cycloheptaamylose columns and reverse-phase HPLC columns. Efforts to purify the individual stereoisomers are currently under way.

Although the reactions leading to the Rh(III) polyphosphate complexes are quite simple to carry out, the yields are generally low owing to competing side reactions. In the case of the preparation of $Rh(H_2O)_4PP$ the low yield is in part due to the intermolecular reaction of the monodentate $Rh(H_2O)_5PP$ complex with a second Rh(III) ion to form Rh_2PP (which passes through the Dowex 1 column) or with a second PP ion to form $Rh(PP)_2$ (which remains bound to the Dowex 1 column after the acid wash). These processes compete with the intramolecular insertion of the uncomplexed phosphoryl group. Likewise, the yield of $Rh(H_2O)_4ADP$ is limited by intermolecular reactions of the β-monodentate $Rh(H_2O)_5ADP$ complex, which compete with bidentate complex formation. The formation of tridentate $Rh(H_2O)_3PPP$ is accompanied by generation of PP, P, $Rh(H_2O)_nP$, and $Rh(H_2O)_4PP$ as determined by ³¹P NMR analysis of the crude reaction mixture. The predominant Rh(III)-containing side product formed during the $Rh(H_2O)_nATP$ reaction passes through the Dowex 50 H⁺ cation-exchange column in the first void volume and is probably $Rh(ATP)_2$.

Unlike the reactions involving $Cr(H_2O)_6^{3+}$, those with $Rh(H_2O)_6^{3+}$ are not amenable to base catalysis. Specifically, attempts to prepare the rhodium complexes in solutions at pH 5 leads to immediate precipitation of the Rh(III), presumably as the hydroxide.

Registry No. **1**, 88905-01-5; **2**, 88905-03-7; **3**, 88905-04-8; **4**, 88979-70-8; Λ-**4**, 88905-07-1; Δ-**4**, 88930-47-6; **5**, 88905-05-9; **6**, 88905-06-0.

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Electrochemical Studies of [Bis(acetylacetone) ethylenediiminato]oxovanadium(IV), VO(acen), and Its Thio Analogue, VS(acen)

R. Seangprasertkij and Thomas L. Riechel*

Although the vanadyl ion Schiff base complex VO(acen) (H_2acen = the Schiff base of acetylacetone and ethylenediamine) has been of interest for many years, its sulfur analogue, VS(acen), has only recently been synthesized.[1,2] The thiovanadyl compound is formed by treating the oxo analogue with B_2S_3 in rigorously dry methylene chloride. The thio complex is quite oxygen sensitive in solution and readily reverts back to the oxo analogue. Electronic, IR, and ESR spectra have been reported for both complexes.[2] Crystallographic studies of VO(acen)[3,4] show its structure to be a rectangular pyramid with the terminal oxygen atom at the apex. The structure of VS(acen) has recently been reported[5] and is quite similar to that of VO(acen) except for the V=O and V=S bond lengths. The V=S bond (2.061 Å) is closer to a single bond in length. Their structures are shown in Figure 1.

We present here an electrochemical study of these compounds and a correlation between their electrochemical behavior and their structures.

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 or a Tektronix Type 549 storage oscilloscope. Controlled-potentional 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 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. Experiments with H_2S gas 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.

Spectrophotometric measurements were made on a Hewlett-Packard 8450A UV/vis spectrophotometer. IR spectra were recorded on a Perkin-Elmer 683 IR spectrophotometer.

Reagents. High-purity dimethyl sulfoxide (0.011% water), acetonitrile (0.003% water), and methylene chloride (0.003% water) were obtained from Burdick and Jackson Laboratories and deoxygenated before use. Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium bromide (Aldrich) and perchloric acid as previously described[6] and used as the supporting electrolyte.

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(5) Sato, M.; Miller, K. M.; Enemark, J. H.; Strouse, C. E.; Callahan, K. P. *Inorg. Chem.* **1981**, *20*, 3571.
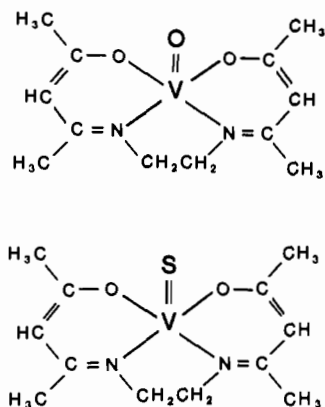(6) Riechel, T. L.; Sawyer, D. T. *Inorg. Chem.* **1975**, *14*, 1869.

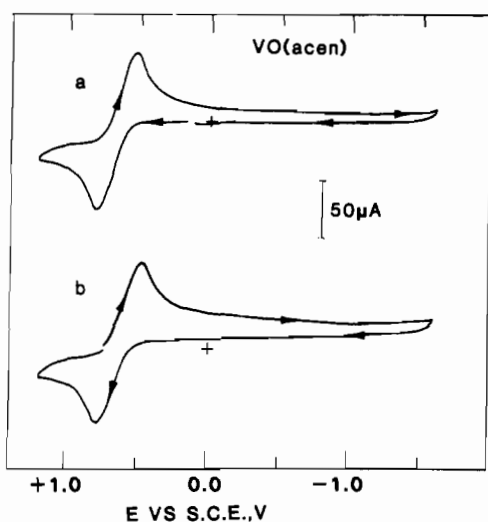**Figure 1.** Structural formulas of VO(acen) (top) and VS(acen) (bottom).

Figure 2. Cyclic voltammograms in 0.1 M TEAP/CH$_2$Cl$_2$ solution (scan rate 0.2 V/s): (a) 1 mM VO(acen); (b) solution a after oxidation at 1.00 V.

[Bis(acetylacetone) ethylenediiminato]oxovanadium(IV), VO(acen).
The ligand bis(acetylacetone) ethylenediimine (H$_2$acen) was prepared by the method of McCarthy, Hovey, Ueno, and Martell[7]. The synthesis of VO(acen) was based on the preparation of Cu(acen) by these workers.[7] To 12.30 g (0.05 mol) of VOCl$_2$ was added 4.0 g (0.10 mol) of NaOH to yield the dark gray precipitate VO(OH)$_2$. The precipitate was washed with water and added to an acetone solution of 11.2 g (0.05 mol) of H$_2$acen. After being refluxed for 1 h, the dark blue complex VO(acen) was precipitated from the acetone solution by addition of water. The product was washed with water and recrystallized from acetone and water. Anal. Calcd: C, 49.85; H, 6.23. Found: C, 49.60; H, 6.26.

[Bis(acetylacetone) ethylenediiminato]thiovanadium(IV), VS(acen).
The VS(acen) complex was prepared by treating VO(acen) with B$_2$S$_3$ in methylene chloride as described by Callahan and Durand.[2] Anal. Calcd: C, 47.24; H, 5.90; S, 10.51. Found: C, 47.23; H, 5.95; S, 10.60.

Results and Discussion

An initial positive scan of a 1 mM solution of VO(acen) in CH$_2$Cl$_2$ gives the cyclic voltammogram shown in Figure 2a. On the basis of the peak height ratio, the couple at 0.66 V vs. SCE appears to be reversible. The oxidation of VO(acen), which occurs at 0.80 V, was studied by controlled-potential coulometry. The solution was oxidized at 1.00 V, and the initial light blue solution of VO(acen) became dark blue at the end of the electrolysis process. The coulometric data indicate that the process is a one-electron transfer. A cyclic

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Table I. Electrochemical and Chemical Reactions

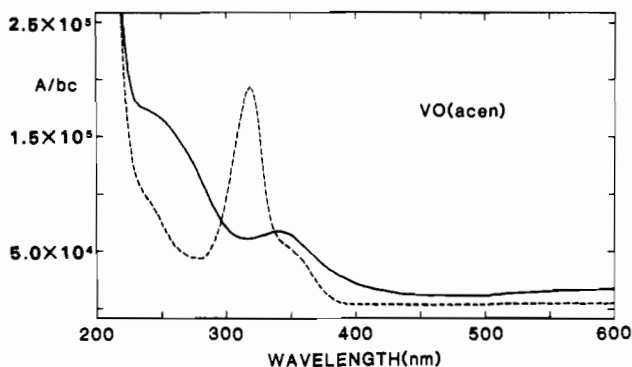| reaction	E_p', V vs. SCE
1. VO(acen) ⇌ VO(acen)$^+$ + e$^-$	0.66
2. VS(acen) + H$_2$O → VO(acen) + H$_2$S	
3. VS(acen) ⇌ VS(acen)$^+$ + e$^-$	0.45
4. VS(acen)$^+$ + H$_2$O → VO(acen)$^+$ + H$_2$S	
5. 2VO(acen)$^+$ + H$_2$S → 2VO(acen) + S^0 + 2H$^+$	

Figure 3. Absorption spectra in CH$_2$Cl$_2$: VO(acen) (- - -); VO(acen) after oxidation at 1.00 V (—).
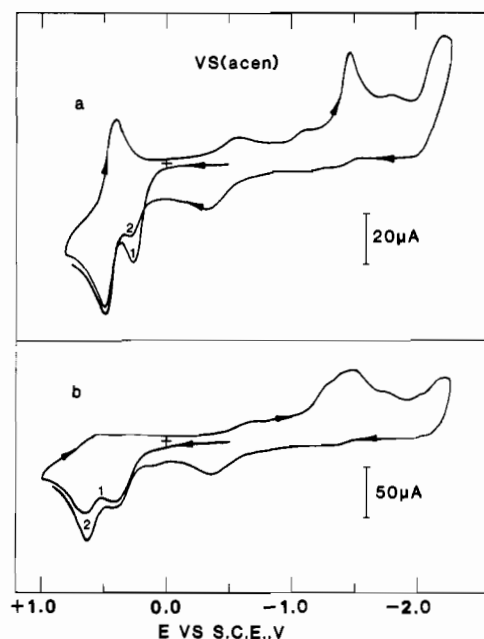

Figure 4. Cyclic voltammograms in 0.1 M TEAP solution (scan rate 0.2 V/s): (a) 1 mM VS(acen) in Me$_2$SO; (b) 1 mM VS(acen) in acetonitrile.

voltammogram recorded after oxidation (Figure 2b) shows that the initial product is stable. (Cyclic voltammograms of the ligand show no peaks in this region; therefore, the oxidation process must involve the metal.) Subsequent controlled-potential reduction at 0.10 V of this solution also is a one-electron process, and the color changes back to light blue. The cyclic voltammogram of this final solution is the same as that of the initial VO(acen) solution (Figure 2a). The reversibility of the oxidation of VO(acen) suggests that the oxidized product is VO(acen)$^+$. The complete redox process is given by reaction 1 in Table I.

UV–Visible spectra corresponding to the electrochemical steps described above are shown in Figure 3. The spectrum of the initial solution of VO(acen) (dashed line) shows an absorption peak at 319 nm and shoulders at 250 and 350 nm. The spectrum of the solution resulting from oxidation at 1.0 V (solid line) shows a broad shoulder at 250 nm and a broad
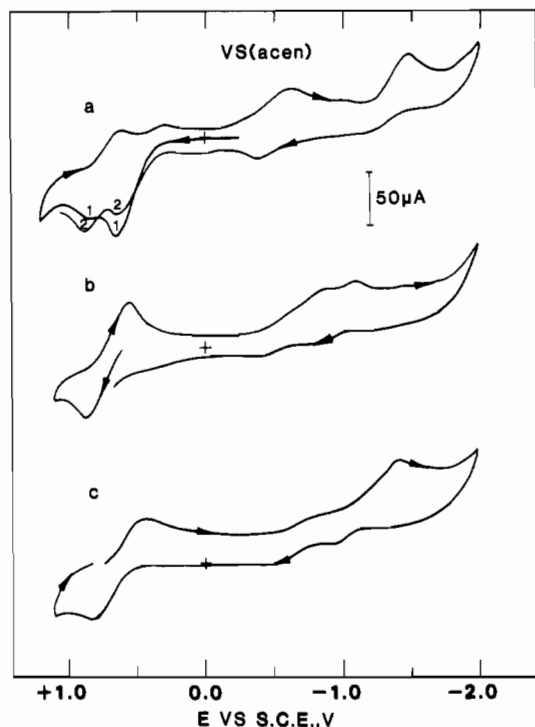
Figure 5. Cyclic voltammograms in 0.1 M TEAP/CH_2Cl_2 solution (scan rate 0.2 V/s): (a) 1 mM VS(acen); (b) solution a after oxidation at 0.75 V; (c) solution b after oxidation at 1.00 V.
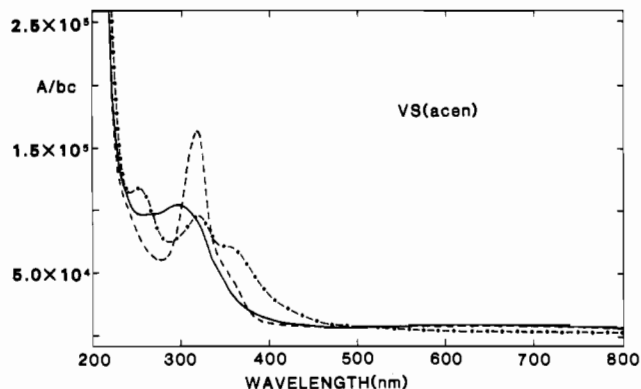

Figure 6. Absorption spectra in CH_2Cl_2 of VS(acen): (a) 1 mM VS(acen) (−·−); (b) solution a after oxidation at 0.75 V (---); (c) solution b after subsequent oxidation at 1.00 V (—).

peak at 340 nm. The spectrum of the final solution (following reduction at 0.10 V) is quite similar to that of the initial VO(acen) solution. Thus, the UV−visible spectral data are consistent with the electrochemical results.

Cyclic voltammetric studies of VS(acen) were carried out in Me_2SO, acetonitrile, and CH_2Cl_2. Figure 4a shows a cyclic voltammogram of 1 mM VS(acen) in Me_2SO. Two oxidation peaks are observed at 0.26 and 0.50 V, with the one at 0.26 V being slightly larger on the first scan. The reduction peak at 0.40 V appears to form a reversible couple with the oxidation peak at 0.50 V, on the basis of peak height ratio. This couple appears at the same potential as a couple observed in the cyclic voltammogram of VO(acen) in Me_2SO. On a second scan the relative peak heights for the two oxidation processes are reversed. The oxidation peak at 0.50 V is much larger.

The cyclic voltammetry of VS(acen) was also studied in acetonitrile. The same two oxidation processes are observed in acetonitrile (Figure 4b), but the peaks are shifted positively to 0.40 and 0.60 V, respectively. The relative peak heights are similar to those in Me_2SO, as are the changes observed on the second scan. That is, the first peak (0.40 V) is larger than the second (0.60 V) on the first scan but smaller on the second scan. These observations suggest the existence of two species in equilibrium. Since the potential of the second oxidation peak in each solvent is the same as that for VO(acen), hydrolysis with residual water may occur to convert VS(acen) to VO(acen). This process is represented by reaction 2 in Table I. This is reasonable as VS(acen) has been reported to revert back to VO(acen) in aqueous solution.[1]

The reaction of VS(acen) with residual water was confirmed by adding several drops of water to the complex in Me_2SO and monitoring the disappearance of the first oxidation peak.

Although the residual water content of CH_2Cl_2 was the same as that in acetonitrile, it did not interfere with the isolation of pure VS(acen). This was confirmed by elemental analysis and IR spectroscopy. The product exhibited a strong band at 598 cm^{-1} (V=S) but no band at 984 cm^{-1} (V=O). Thus, CH_2Cl_2 was chosen for further electrochemical study of VS(acen) in order to minimize the formation of VO(acen).

An initial positive cyclic voltammetric scan of 1 mM VS-(acen) in CH_2Cl_2 is shown in Figure 5a. The oxidation of VS(acen) occurs at 0.66 V while the slight peak at 0.84 V indicates that only a trace of VO(acen) has been formed. The second scan shows that more VO(acen) has been produced as in Me_2SO and acetonitrile. The reduction peak at 0.64 V, which corresponds to VO(acen)$^+$, is smaller in CH_2Cl_2 than in Me_2SO because in CH_2Cl_2 the dominant species is VS(acen) rather than VO(acen). The UV−visible spectrum of VS(acen) is CH_2Cl_2 is shown in Figure 6 (dot−dash line). Absorption peaks appear at 258 and 320 nm, and a shoulder appears at 355 nm.

The oxidation of VS(acen) was carried out by controlled-potential electrolysis at 0.75 V. The coulometric data were inconsistent, giving between 0.5 and 0.6 electron per vanadium depending upon the age of the solution. This variation corresponds to the hydrolysis of VS(acen) to VO(acen). The cyclic voltammogram of the resulting solution is shown in Figure 5b and verifies the presence of VO(acen) (Figure 2a). The UV−visible spectrum of this solution (Figure 6, dashed line) is nearly identical with that of VO(acen) (Figure 3, dashed line). The yellow-orange color of the initial VS(acen) solution became light blue after oxidation, which agrees with the color of the initial VO(acen) solution. The subsequent oxidation of VO(acen) was carried out by holding the potential at 1.00 V. The resulting solution exhibits a voltammogram as shown in Figure 5c. These data clearly show the presence of VO(acen)$^+$, as in Figure 2b. The UV−visible spectra of the two solutions are similar but not identical (solid lines in Figures 3 and 6).

The cyclic voltammetry of VS(acen) was also studied at fast scan rates utilizing a storage oscilloscope to collect the data. Parts a and b of Figure 7 show cyclic voltammograms of 1 mM solutions of VO(acen) and VS(acen), respectively, in CH_2Cl_2 at normal scan rates (200 mV/s). They are comparable to the voltammograms of Figures 2a and 5a. Figure 7c shows cyclic voltammograms of a 1 mM VS(acen) solution in CH_2Cl_2 at scan rates of 2, 5, 10, and 20 V/s. It can be clearly seen that at fast scan rates the oxidation of VS(acen) approaches reversibility on the basis of peak height ratios. Although the peak potential separation is larger than the theoretical value, it is clear that the reduction peak at 0.30 V is due to VS(acen)$^+$, not VO(acen)$^+$. Thus, we suggest that the oxidation of VS(acen) is reversible (as given by reaction 3, Table I) but VS(acen)$^+$ is too unstable to be detected at normal scan rates.

Considering only the above data, it is unclear how bulk oxidation of VS(acen) can lead to VO(acen), which requires no oxidation-state change. Reactions 4 and 5 in Table I represent a possible explanation. It has been demonstrated that VS(acen) undergoes hydrolysis to produce VO(acen) and
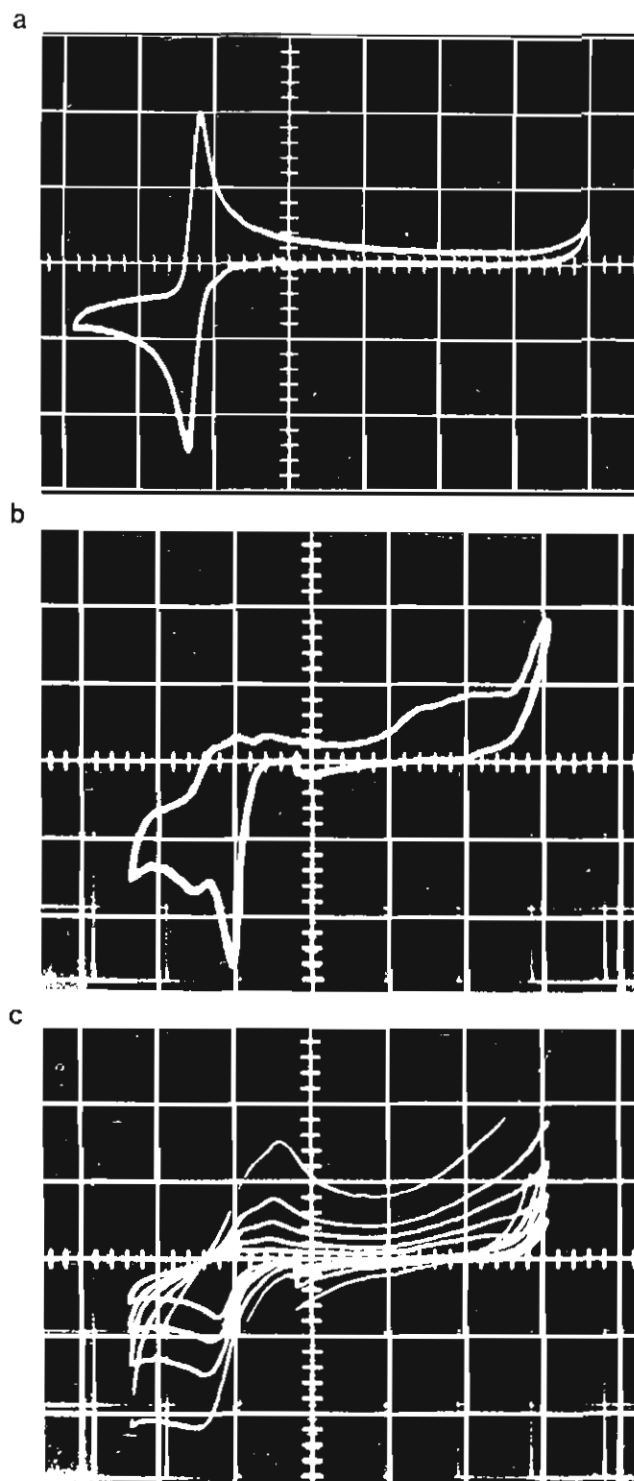
a

b

c

Figure 7. Oscilloscope traces of cyclic voltammograms in 0.1 M TEAP/CH$_2$Cl$_2$: (a) 1 mM VO(acen) (scan rate 0.2 V/s); (b) 1 mM VS(acen) (scan rate 0.2 V/s); (c) 1 mM VS(acen) (scan rates 2, 5, 10, and 20 V/s).

that VS(acen) can be oxidized to VS(acen)$^+$. We propose (reaction 4) that VS(acen)$^+$ undergoes hydrolysis to give VO(acen)$^+$ in a fashion similar to that of the reaction involving the two vanadium(IV) species. This produces H$_2$S, a powerful reducing agent. We further propose (reaction 5) that, in the presence of H$_2$S, VO(acen)$^+$ is spontaneously reduced to VO(acen), vanadium(IV).

That H$_2$S may function as suggested above was shown by passing H$_2$S gas for a few seconds through a solution of VO-(acen)$^+$. Figure 8a shows a cyclic voltammogram of the solution after treatment with H$_2$S. The initial anodic scan shows

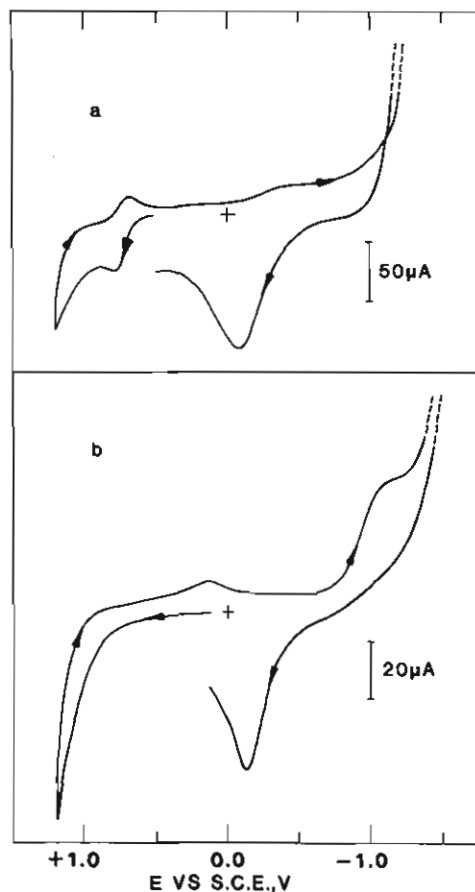**Figure 8.** Cyclic voltammograms in 0.1 M TEAP/CH$_2$Cl$_2$ (scan rate 0.2 V/s): (a) VO(acen)$^+$ solution after bubbling with H$_2$S(g); (b) solution of supporting electrolyte alone after bubbling with H$_2$S(g).

clearly that VO(acen) has been regenerated. The solution color change is also consistent with this conclusion. Figure 8b shows a cyclic voltammogram of H$_2$S in supporting electrolyte. The hydrogen sulfide appears to have again undergone a spontaneous reaction. No attempt to identify the products of H$_2$S oxidation has been made, but the two voltammograms show the same oxidation peak at −0.15 V and a dominant reduction process more negative than −1.00 V. In both experiments small white particles were produced that may be elemental sulfur. We have suggested this in reaction 5.

Conclusion

Both VO(acen) and VS(acen) are reversibly oxidized by 1 electron per vanadium. The oxidation of VS(acen) is somewhat easier than that of VO(acen), probably due to the lower electronegativity of sulfur as compared to oxygen. The similarities of these processes are consistent with the similar structures of these compounds, but the long V═S bond distance makes the sulfur atom quite labile in both vanadium(IV) and -(V) complexes. Thus, VS(acen) exchanges with residual water even in rigorously dry solvents but can be studied in CH$_2$Cl$_2$, the solvent in which it is synthesized. Fast scan rate studies indicate the behavior of VS(acen) and VS(acen)$^+$ that would be observed if all water could be eliminated from the solvent. The oxidized product, VS(acen)$^+$, is much less stable than VS(acen), and the reaction with water produces the powerful reducing agent H$_2$S. Thus, the presence of any vanadium(V) species derived from VS(acen) oxidation is expected to have only a fleeting existence.