Electrochemical Investigations of the Complexes Resulting from the Acid-Promoted Deoxygenation and Dimerization of (*N*,*N*′-Ethylenebis(salicylideneaminato))oxovanadium(IV)[‖]

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Electrochemical confirmation that (*N*,*N*′-ethylenebis(salicylideneaminato))oxovanadium(IV), VO(salen), reacts with trifluoromethanesulfonic acid (CF_3SO_3H) or triphenylmethyl tetrafluoroborate ($Ph_3C(BF_4)$) to form a deoxygenated complex, $V^{IV}(salen)^{2+}$, and a μ-oxodinuclear complex, $[(salen)VOV(salen)]X_2$, ($X = CF_3SO_3^-$ or BF_4^-) is presented. Cyclic voltammograms of VO(salen) in the presence of CF_3SO_3H or $Ph_3C(BF_4)$ exhibit reversible waves with formal potentials near 0.5 and 0.8 V (vs Ag/AgCl). The cathodic wave at 0.5 V is argued to arise from the combined reduction of $V(salen)^{2+}$ and the μ-oxo dimeric complex and the wave at 0.8 V from the oxidation of the $V(salen)^{2+}$ complex. The diffusion coefficients of these three complexes in acetonitrile were determined. The dimerization of VO(salen) is initiated by deoxygenation of the V=O center by H^+ or Ph_3C^+ to produce $V(salen)^{2+}$ which enters into an equilibrium with a second VO(salen) complex to produce the μ-oxo dimer. The kinetics of the second order dimerization reaction were monitored, and the equilibrium contant for the formation of the μ-oxo dimer in acetonitrile was evaluated as 0.7 mM^{-1}.

The chemistry of vanadium(IV) is dominated by the stable oxovanadium cation (VO^{2+}) which remains intact during many reactions.[1] The deoxygenation of oxo complexes of vanadium(IV) to form six-coordinate vanadium(IV) complexes usually enhances their reactivity.[2] Since vanadium(V) is a strong oxidant and vanadium(III) and, sometimes, V(IV) can be oxidized by molecular oxygen, redox reactions involving the V(IV)/V(III) and V(V)/V(IV) couples are of interest in relation to the autoxidation of organic molecules. Indeed, oxovanadium(IV) derivatives have been used as catalysts in the epoxidation of olefins and in the oxidation of sulfides with peroxides.[3]

It was previously reported that bis(acetylacetonato)oxovanadium(IV), $VO(acac)_2$, acts as an excellent catalyst in the oxygen-driven oxidative polymerization of diphenyl disulfide to produce poly(*p*-phenylene sulfide).[4] These studies on the polymerization process have revealed that stoichiometric oxygen consumption occurs during the polymerization. However, mechanistic analysis of the redox processes involved in the catalytic cycle was made difficult because of the lability of the β-diketone ligand.[5]

In this report we describe the electron transfer chemistry of a more stable model of the acetylacetonato catalyst. The model complex is VO(salen) (salen = *N*,*N*′-ethylenebis(salicylideneamine). The present study revealed that VO(salen) is deoxygenated in strongly acidic non-aqueous media and the deoxygenated complex reacts with VO(salen) itself to form a μ-oxo dinuclear vanadium complex. Electrochemical measurements were used to define the redox properties of the complexes involved and to monitor the slow dimerization reaction. The oxidation of VO(salen) by oxygen to produce $VO(salen)^+$ proved feasible in the presence of acid. The behavior of VO(salen) in acidic media in the presence of O_2 is of interest with regard to the mechanism by which it and its bis(acetylacetonato) analog act as autoxidation catalysts.

Bonadies et al.[6] have previously reported the redox properties of VO(salen) in acetonitrile in the presence of perchloric acid and provided evidence for what they took to be the disproportionation of VO(salen) to $VO(salen)^+$ and a vanadium(III) species. The V(III) complex was not fully characterized, and the final products obtained seem likely to have been affected by the H_2O contained in the perchloric acid solutions employed. This report offers an account of the reactions which ensue in acidified solutions of VO(salen) in essentially anhydrous acetonitrile. The results suggested that, in the absence of H_2O, proton-induced deoxygenation rather than disproportionation dominates the chemistry.

Experimental Section

Apparatus and Procedures. Electrochemical measurements were carried out in a conventional two-compartment cell. Solutions were kept under an atmosphere of dry argon. A conventional gas scrubber was used to remove traces of oxygen and water from the argon. A platinum disk or glassy-carbon disks were used as working electrodes and polsihed before each experiment with 0.05-μm alumina paste. The auxiliary electrode, a coiled platinum wire, was separated from the working solution

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(1) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Interscience: New York, 1987. (b) Boas, L. V.; Pessoa, J. C. In *Comprehensive Coordination Chemistry, The Synthesis, Reactions, Properties & Applications of Coordination Compounds*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 3, Chapter 33.

(2) (a) Swinehart, J. H. *J. Chem. Soc., Chem. Commun.* **1971**, 1443. (b) Pasquali, M.; Filho, A. T.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1975**, 534. (c) Behzadi, K.; Thompson, A. *J. Less-Common Met.* **1987**, *128*, 281.

(3) (a) Curci, R.; Furia, F. D.; Testi, R.; Modena, G. *J. Chem. Soc., Perkin Trans.* **1974**, *2*, 753. (b) Howard, J. A.; Tait, J. C.; Yamada, T.; Chenier, J. H. B. *Can. J. Chem.* **1981**, *59*, 2184.

(4) (a) Tsuchida, E.; Yamamoto, K.; Jikei, M.; Nishide, H. *Macromolecules* **1989**, *22*, 4138. (b) Yamamoto, K.; Tsuchida, E.; Nishide, H.; Yoshida, S.; Park, Y.-S. *J. Electrochem. Soc.* **1992**, *139*, 2401. (c) Tsuchida, E.; Nishide, H.; Yamamoto, K.; Jikei, M.; Oyaizu, K. *Macromolecules* **1993**, *26*, 3432. (d) Tsuchida, E.; Yamamoto, K.; Jikei, M.; Nishide, H. *Macromolecules* **1990**, *23*, 930. (e) Yamamoto, K.; Jikei, M.; Oi, K.; Nishide, H.; Tsuchida, E. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1359. (f) Tsuchida, E.; Yamamoto, K.; Nishide, H.; Yoshida, S.; Jikei, M. *Macromolecules* **1990**, *23*, 2101.

(5) (a) Patel, K. S.; Kolawole, G. A. *J. Coord. Chem.* **1986**, *15*, 137. (b) Patel, K. S.; Kolawole, J. *Coord. Chem.* **1986**, *15*, 137. (c) Selbin, J.; Maus, G.; Johnson, D. L. *J. Inorg. Nucl. Chem.* **1967**, *29*, 1735. (d) Selbin, J. *Chem. Rev.* **1965**, *65*, 153. (e) Selbin, J. *Coord. Chem. Rev.* **1966**, *1*, 293.

(6) (a) Bonadies, J. A.; Butler, W. M.; Pecoraro, V. L.; Carrano, C. J. *Inorg. Chem.* **1987**, *26*, 1218. (b) Bonadies, J. A.; Pecoraro, V. L.; Carrano, C. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1218.

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by a fine-porosity frit. The reference electrode was a commercial Ag/AgCl electrode immersed in a salt bridge consisting of 0.1 M tetrabutylammonium trifluoromethanesulfonate in acetonitrile, which was placed in the main cell compartment. The formal potential of the ferrocenium/ferrocene couple was 0.47 V vs this reference electrode. All potentials are quoted with respect to this Ag/AgCl reference electrode. A Princeton Applied Research Model 173 potentiostat and a Model 175 universal programmer were employed with a Houston Instruments Model 2000 recorder to obtain voltammograms.

Electron paramagnetic resonance spectra were recorded on a JEOL RE-2XG spectrometer, and Mn^{2+}/MgO was used to calibrate the magnetic field. A cylindrical quartz cell with a diameter of 2 mm was used as a sample tube. UV–visible spectra were obtained with a Shimadzu UV-2100 Spectrophotometer. Infrared spectra were obtained using a Perkin-Elmer 1600 spectrometer having 4-cm^{-1} resolution. Samples were prepared in potassium bromide pellets. A ^{51}V-NMR spectrum was obtained using a JEOL 400-MHz FT-NMR GXS400. Neat $VOCl_3$ was used as the reference sample. Mass spectra were obtained with a JEOL Model JMS-DX300 instrument by direct exposure techniques with an ionization energy of 20 eV. A FABMAS spectrum was obtained using a VGZAB-HF spectrometer with *m*-nitrobenzyl alcohol as the matrix material.

Materials and Solvents. *N,N'*-Ethylenebis(salicylideneamine) (salen) was prepared by standard literature methods. VO(salen) was prepared from tris(acetylacetonato)vanadium(III), salen, and air[7] and purified by recrystallization from dichloromethane–methanol. VCl_2(salen) was prepared from VO(salen) and thionyl chloride.[8] All solvents were purified by distillation and stored over molecular sieves. Tetrabutylammonium tetrafluoroborate of electrochemical grade was obtained from Southwestern Analytical Chem. Inc. Tetrabutylammonium trifluoromethanesulfonate was prepared from tetrabutylammonium bromide and trifluoromethanesulfonic acid and purified by recrystallization from dichloromethane–diethyl ether. Triphenylmethyl tetrafluoroborate ($Ph_3C(BF_4)$), trifluoromethanesulfonic acid (CF_3SO_3H), and silver trifluoromethanesulfonate (CF_3SO_3Ag) were used as received from commercial sources.

(*N,N'*-Ethylenebis(salicylideneaminato))oxovanadium(V) Tetrafluoroborate, [V^{V}O(salen)]BF$_4$ (1). Oxidation of VO(salen) by oxygen does not take place in the absence of acid, but it proceeds in the presence of $Ph_3C(BF_4)$. The vanadium(V) complex was produced by bubbling oxygen through a solution prepared by dissolving VO(salen) (0.126 mmol, 0.042 g) in 50 mL of acetonitrile to which an equimolar amount of $Ph_3C(BF_4)$ (0.041 g) was added. After being stirred under oxygen for 1 week, the solution was evaporated to give a black powder. Recrystallization from acetonitrile–dichloromethane gave the pure product as dark blue crystals. Anal. Calcd for [VO(salen)]BF$_4$: C, 45.75; H, 3.36; N, 6.67. Found: C, 45.14; H, 3.32; N, 6.63. IR/cm^{-1}: 1124, 1083, 1033 (ν_{B-F}), 973 ($\nu_{V=O}$). The use of CF_3SO_3H in place of $Ph_3C(BF_4)$ also enabled the autoxidation of VO(salen) to proceed to produce the corresponding product, [VO(salen)](CF_3SO_3). The ^{51}V-NMR spectrum (400 MHz; solvent CH_3CN; standard $VOCl_3$) showed a distinct signal at –598 ppm, which was ascribed to vanadium(V).[9]

(μ-Oxo)bis[(*N,N'*-ethylenebis(salicylideneaminato))vanadium(IV) Tetrafluoroborate, [VOV(salen)$_2$](BF$_4$)$_2$ (2). VO(salen) (0.631 mmol, 0.21 g) was dissolved in dichloromethane (20 mL). An equimolar amount of $Ph_3C(BF_4)$ (0.21 g) in dichloromethane (5 mL) was added slowly to the solution in a pure argon atmosphere. A black powder precipitated from the reaction mixture after a few minutes and was isolated under anaerobic conditions. The yield was >90%. Anal. Calcd for [{V(salen)}$_2$(μ-O)](BF$_4$)$_2$: C, 46.64; H, 3.42; N, 6.80. Found: C, 46.58; H, 3.66; N, 6.84. IR/cm^{-1} 1124, 1183, 1033 (ν_{B-F}). FABMAS: *m/z* 650, 333, 316. The tetrafluoroborate salt is slightly soluble in dichloromethane.

(*N,N'*-Ethylenebis(salicylideneaminato))vanadium(IV) Tetrafluoroborate, V(salen)(BF$_4$)$_2$ (3). A dilute solution of VO(salen) (0.375 mmol, 0.125 g) in dichloromethane (100 mL) was slowly added to a 10-fold molar excess of $Ph_3C(BF_4)$ (3.75 mmol, 1.24 g) in dichloromethane (50 mL) in a pure argon atmosphere. A pale blue powder precipitated from the reaction mixture after a few minutes and was isolated under anaerobic conditions. IR/cm^{-1}: 1084, 1038 (ν_{B-F}). MS: *m/z* 316. The deoxygenation of VO(salen) by Ph_3C^+ was confirmed by the absence of the stretching band of the V=O unit in the IR spectrum. The deoxygenation was also supported by the ESR spectrum, which matched that obtained from the complex prepared by reacting VCl_2(salen) with CF_3SO_3Ag in acetonitrile to precipitate AgCl.

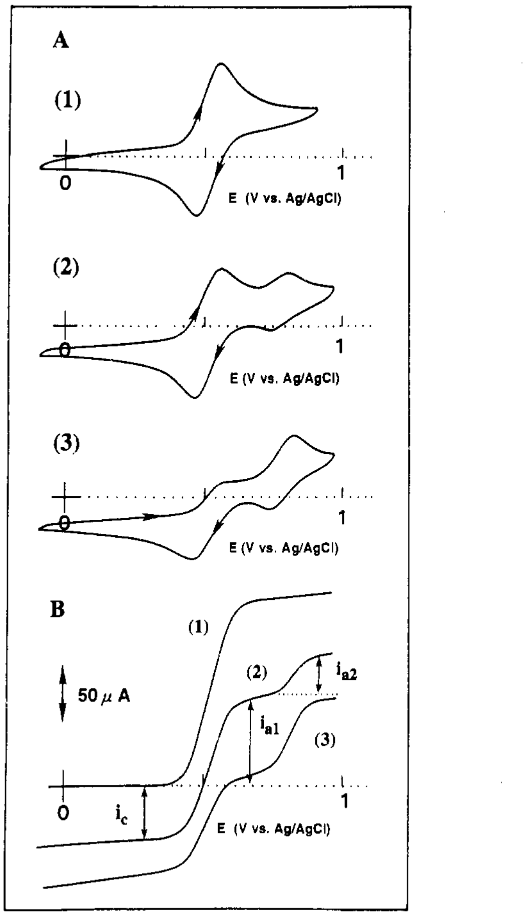

Figure 1. (A) Steady-state cyclic voltammograms for a 1 mM solution of VO(salen) in anaerobic anhydrous CH_3CN. The supporting electrolyte contained 0.1 M tetrabutylammonium tetrafluoroborate to which was added (1) 0, (2) 1.0, (3) 2.5 mmol/L of $Ph_3C(BF_4)$. Scan rate = 100 mV s^{-1}. A 5-mm-diameter glassy-carbon electrode was used. (B) Current-potential curves for the three solutions used in part A recorded at the same glassy-carbon disk electrode rotated at 1000 rpm and scanned at 5 mV s^{-1}.

Results and Discussion

Electrochemistry of VO(salen) in the Absence and in the Presence of Acid. In order to expose the redox chemistry of the various vanadium complexes and to compare with the previously reported results,[6] the electrochemical responses of the complexes were recorded in the absence and in the presence of added H$^+$ or Ph_3C^+ cations. The latter carbenium cation is commonly used as a strong Lewis acid in organic solvents.[10] Figure 1A shows how cyclic voltammograms for VO(salen) change as Ph_3C^+ cations are added to the solution. The addition causes a new, reversible redox couple to develop at more positive potentials at the expense of the initial couple. Current–potential curves recorded at a rotating glassy-carbon disk electrode for the same three solutions are shown in Figure 1B. These curves demonstrate that the addition of trityl cation generates a reducible species and also produces a composite anodic–cathodic wave which reflects the presence of both oxidizable and reducible species with the same, or nearly the same, formal potentials. When 2 mol (or more) of

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(7) Bonadies, J. A.; Carrano, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 4088.

(8) Pasquali, M.; Marchetti, F.; Floriani, C. *Inorg. Chem.* **1979**, *18*, 2401.

(9) (a) Hibbert, R. C.; Logan, N.; Howarth, O. W. *J. Chem. Soc., Dalton Trans.* **1986**, 369. (b) Naumann, F.; Rehder, D.; Pank, V. *Inorg. Chim. Acta* **1984**, *84*, 117. (c) Divore, D. D.; Lightenhan, J. D.; Takusagawa, F.; Maatta, E. A. *J. Am. Chem. Soc.* **1987**, *109*, 7408. (d) Rehder, D. *Magn. Res. Rev.* **1984**, *9*, 125.

(10) (a) Kobayashi, S.; Sagawa, Y.; Akamatsu, H.; Mukaiyama, T. *Chem. Lett.* **1988**, 1777. (b) Mukaiyama, T.; Sagawa, T.; Kobayashi, S. *Chem. Lett.* **1987**, 2169.

Table 1. Diffusion Coefficients and Molar Absorptivities of Several Vanadium–salen Complexes in CH_3CN

complex	abbr	10^5 D,[a] $cm^2\ s^{-1}$	$10^{-3}\ \epsilon_{max}$,[b] $M^{-1}\ cm^{-1}$	λ_{max},[c] nm	$10^{-3}\ \epsilon_{567}$,[d] $M^{-1}\ cm^{-1}$
VO(salen)	VO	1.3	0.139	585	0.127
$VO(salen)^+$		1.0	1.39	568	1.37
$V(salen)^{2+}$	V^{2+}	0.41	0.159	557	0.159
$[(salen)VOV(salen)]^{2+}$	VOV^{2+}	0.92	2.05	567	2.05
$[(salen)VOV(salen)]^{3+}$	VOV^{3+}	0.90			

[a] Diffusion coefficient measured in 0.1 M tetrabutylammonium tetrafluoroborate in CH_3CN. [b] Molar absorptivity at the wavelength of maximum absorption. [c] Wavelength of maximum absorption. [d] Molar absorptivities at the λ_{max} value for the dimeric complex.

Ph_3C^+ per mole of VO(salen) is added to the solution, the composite wave is almost eliminated, and it is replaced by separated oxidation and reduction waves (Figure 1B, curve 3). Behavior essentially similar to that shown in Figure 1 was obtained by Bonadies et al.[6] by addition of up to 2.0 equiv of $HClO_4$ (presumably along with some H_2O) to acetonitrile solutions of VO(salen).

The single anodic process obtained at 0.55 V with VO(salen) in the absence of Ph_3C^+ or H^+ ions (Figure 1A, curve 1; Figure 1B, curve 1) corresponds to the reversible oxidation to $VO(salen)^+$, half-reaction 1. The independently prepared and isolated $VO(salen)^+$ complex (see Experimental section) exhibited a single, reversible reduction wave at the same potential (0.55 V), as expected. Levich plots[11] of plateau current at the rotating disk electrode vs the electrode (rotation rate)$^{1/2}$ were measured for both VO(salen) and $VO(salen)^+$. The plots were linear and their slopes corresponded to the diffusion coefficients listed in Table 1. The somewhat smaller diffusion coefficient of the charged $VO(salen)^+$ complex probably reflects its more extensive solvation.

$$VO(salen) - e^- \rightleftharpoons VO(salen)^+ \qquad (1)$$

No reduction of VO(salen) occurs before ca. −1.6 V where an irreversible reduction occurs which is believed to involve elimination of the oxo group from the coordination sphere of the vanadium.[12]

As can be seen in Figure 1B, curve 3, the addition of a 2.5-fold molar excess of Ph_3C^+ (or H^+) to the solution of VO(salen) generates a new species which is oxidized near 0.8 V and reduced at 0.53 V with a cathodic plateau current about half as large as the original anodic plateau current. The reduction happens to occur at almost the same potential where $VO(salen)^+$ is reversibly reduced. Bonadies et al.[6] observed essentially similar behavior upon the addition of 2.0 mol of $HClO_4$ per mole of VO(salen), and this coincidence of potentials led them to conclude that the addition of acid provokes the disproportionation of VO(salen) to $VO(salen)^+$ and a V(III) complex. However, we observed that the magnitudes of the cathodic plateau currents produced by the addition of 2.0 mol of H^+ per mole of VO(salen) were essentially the same as when more than 2.0 mol of H^+ was added. This behaivor is inconsistent with an acid-induced disproportionation because the VO(salen) produced by a one-electron electroreduction of $VO(salen)^+$ should also disproportionate in the presence of protons so that a net two-electron reduction of $VO(salen)^+$ would be observed even if the electrode reaction itself involved only a single electron. Thus we sought an interpretation of the results obtained in anhydrous media which did not involve disproportionation of VO(salen).

We wish to propose an explanation based on the presence of the deoxygenated complex, $V(salen)^{2+}$, to account for the changes in electrochemical behavior observed when acid is added to solutions of VO(salen). In Figure 2 are shown cyclic and rotating disk voltammograms for a solution prepared by dissolving the deoxygenated salt, $V(salen)(BF_4)_2$, (see Experimental Section) in anhydrous acetonitrile. Two reversible couples are obtained near 0.8 and 0.53 V, and the rotating disk voltammogram contains well-separated reduction and oxidation waves of equal magnitude. Note the close correspondence between the rotating disk voltammogram in Figure 2B and that in Figure 1B, curve 3. The oxidation wave near 0.8 V in Figure 2B is reasonably assignable to half-reaction 2 because the removal of the oxo group from VO(salen) would be expected to shift the oxidation of the complex to more positive potentials.

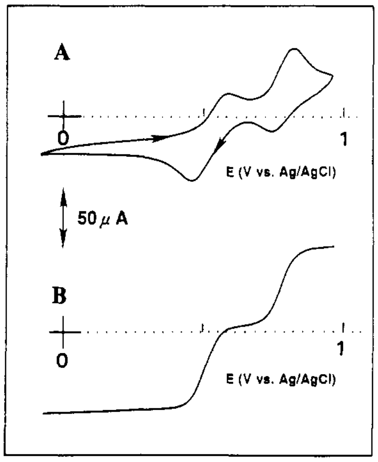

Figure 2. Steady-state cyclic voltammogram (A) and rotating disk current–potential curve (B) for a 1 mM solution of $V(salen)^{2+}$ in CH_3CN. Other conditions were as in Figure 1.

$$V(salen)^{2+} - e^- \rightleftharpoons V(salen)^{3+} \qquad (2)$$

The cathodic wave near 0.5 V in Figure 2B has the magnitude of a one-electron reduction which is assigned to half-reaction 3.

$$V(salen)^{2+} + e^- \rightleftharpoons V(salen)^+ \qquad (3)$$

That the deoxygenated $V(salen)^{2+}$ complex is more readily reduced than the VO(salen) complex (which exhibits no cathodic wave before −1.6 V) is not surprising. Both the $V(salen)^{2+}$ and $V(salen)^+$ complexes probably contain CH_3CN molecules in their coordination spheres, e.g., $V(NCCH_3)_2(salen)^{2+/+}$, and more facile electron transfer and electrochemical reversibility of such six-coordinate, deoxygenated V(IV)/V(III) couples is also obtained with the analogous $V(acac)_3{}^{+/0}$ couple.[12] Thus, we propose that the addition of 2 mol or more of protons or trityl cations per mole of vanadium to anhydrous solutions of VO(salen) leads to deoxygenation rather than disproportionation and produces $V(NCCH_3)_2(salen)^{2+}$ which is both oxidizable and reducible in one-electron reversible steps at well-separated potentials.[13]

Levich plots for both the cathodic and anodic plateau currents in Figure 2B were linear and corresponded to a diffusion coefficient of $4.1 \times 10^{-6}\ cm^2\ s^{-1}$ for $V(NCCH_3)_2(salen)^{2+}$. This smaller diffusion coefficient, compared with the values for the other complexes in Table 1, is presumably the result of very strong solvation of the doubly charged cation as well as the increase in size which results when an oxo group is replaced by two CH_3CN molecules in the coordination sphere of the complex. Whatever the reason for the smaller diffusion coefficient of the deoxygenated complex, it accounts for the decrease in plateau currents that accompany the addition of acid to solutions of VO(salen).

Spectroscopic Observations. In addition to the electrochemical evidence in Figure 1 and 2, spectroscopic experiments were also

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(11) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley & Sons: New York, 1980; Chapter 8.

(12) (a) Nawi, M. A.; Riechel, T. L. *Inorg. Chem.* **1981**, *20*, 1974. (b) Nawi, M. A.; Tiechel, T. L. *Inorg. Chem.* **1982**, *21*, 2268. (c) Seangprasertkij, R.; Riechel, T. L. *Inorg. Chem.* **1984**, *23*, 991.

(13) The isolated deoxygenated complex is extremely moisture sensitive, which has thus far prevented precise elementary analyses or crystallographic characterization.

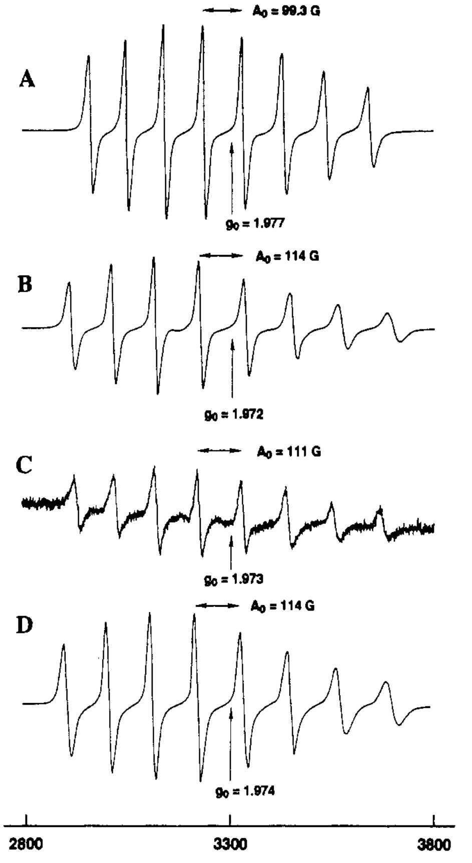

Figure 3. ESR spectra: (A) 1 mM VO(salen); (B) 1 mM VO(salen) + 2.5 mM $Ph_3C(BF_4)$; (C) 0.1 mM VCl_2(salen) + 10 mM CF_3SO_3Ag; (D) 1 mM [V(salen)]$(BF_4)_2$. Spectra were recorded at room temperature with anaerobic CH_3CN as solvent.

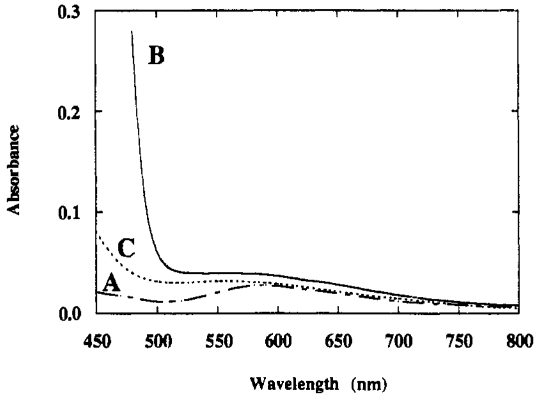

Figure 4. Visible spectra: (A) 1 mM VO(salen); (B) 1 mM VO(salen) + 2.5 mM $Ph_3C(BF_4)$; (C) 1 mM [V(salen)]$(BF_4)_2$. The solvent was anhydrous CH_3CN.

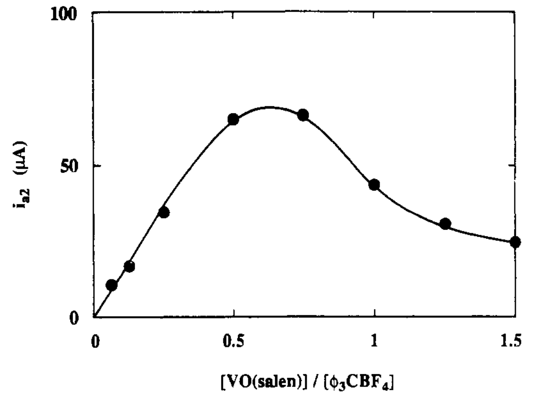

Figure 5. Rotating disk plateau current for the second anodic wave in mixtures of VO(salen) and $Ph_3C(BF_4)$. The concentration of Ph_3C^+ was constant, 2.0 mM. Electrode rotation rate = 1000 rpm. Other conditions were as in Figure 1.

carried out to examine the behavior of mixtures of VO(salen) and acid. In Figure 3 are presented ESR spectra of various complexes in anhydrous acetonitrile at room temperature. Curve A is the ESR spectrum of a 1 mM solution of VO(salen). The distinct eight-line spectrum, with the g_0 value and hyperfine coupling constant, A_0, given in Figure 3, originates in the paramagnetic V(IV) center. Addition of $Ph_3C(BF_4)$ to the solution caused the ESR spectrum to change until, with a 2.5-fold (or greater) molar excess of $Ph_3C(BF_4)$, a new stable spectrum resulted (Figure 3, curve B). Essentially the same spectrum was also obtained by mixing VCl_2(salen) with excess $AgCF_3SO_3$ (Figure 3, curve C) or by dissolving the independently prepared [V(salen)]$(BF_4)_2$ salt in anhydrous acetonitrile (Figure 3, curve D). The spectrum in curve B also resulted when CF_3SO_3H instead of $Ph_3C(BF_4)$ was added to the VO(salen) solution. The spectra in parts B–D of Figure 3 are assigned to the V$(NCCH_3)_2$(salen)$^{2+}$ complex. The increase in A_0 which accompanies the removal of the oxo group is the expected result of increasing the density of the unpaired electron on the vanadium(IV) center.

Bonadies et al.[6] reported that the ESR spectrum of VO(salen) disappeared when 2 equiv of $HClO_4$ per mole of complex were added to anaerobic solutions in acetonitrile. It seems possible that the water added along with the $HClO_4$ in these experiments may have been responsible for the lack of appearance of the ESR spectrum of V(salen)$^{2+}$ because we observed that addition of H_2O to anhydrous solutions of V(salen)$^{2+}$ caused the ESR signal in Figure 3, curve D, to diminish substantially.

The visible spectra of VO(salen) solutions in anhydrous acetonitrile also undergo small changes when protons or trityl cations are added as shown in Figure 4. The spectra obtained in the presence of excess protons or by dissolution of V(salen)$(BF_4)_2$ are attributable to V(salen)$^{2+}$. The deoxygenation reaction believed to be responsible for the generation of V(salen)$^{2+}$ from VO(salen) is

$$\mathrm{VO(salen)} + 2\mathrm{H}^+ \ (\text{or } 2\mathrm{Ph_3C^+}) \rightarrow \mathrm{V(salen)^{2+}} + \mathrm{H_2O}\ (\text{or } \mathrm{Ph_3COCPh_3}) \quad (4)$$

Electrochemistry of VO(salen) in the Presence of Equimolar (or Less) Acid. The rotating disk voltammogram obtained when only 1 mol of acid per mole of complex was added to a solution of VO(salen) was shown in Figure 1B, curve 2. The pattern is qualitatively what might be anticipated on the basis of reaction 4 and electrochemistry already described if the acidified solution contained a mixture of V(salen)$^{2+}$ and VO(salen) with the apparently composite wave attributed to the near coincidence of the formal potentials of the VO(salen)$^{+/0}$ and V(salen)$^{2+/+}$ couples. However, quantitative measurements of the magnitudes of the three plateau currents (two anodic and one cathodic) in curve 2 of Figure 1B do not confirm such a simple interpretation. Thus, the anodic plateau current for the wave which appears at the potential corresponding to the oxidation of V(salen)$^{2+}$ to V(salen)$^{3+}$ (the current labeled i_{a2} in curve 2 of Figure 1B) is significantly smaller than the cathodic plateau current labeled i_c which appears at the potential corresponding to the reduction of the same complex to V(salen)$^+$. To examine the behavior of the plateau current for the second anodic wave in more detail, the magnitude of i_{a2} was measured as VO(salen) was added to a 2 mM solution of Ph_3C^+ in anhydrous acetonitrile. The plot of i_{a2} vs the molar ratio of VO(salen) to Ph_3C^+ in the solution, shown in Figure 5, has a maximum near 0.5 as expected if the oxidizable species responsible for i_{a2} were V(salen)$^{2+}$ produced in reaction 4. However, the decrease in i_{a2} when additional VO(salen) is added to the solution in which all of the Ph_3C^+ has been

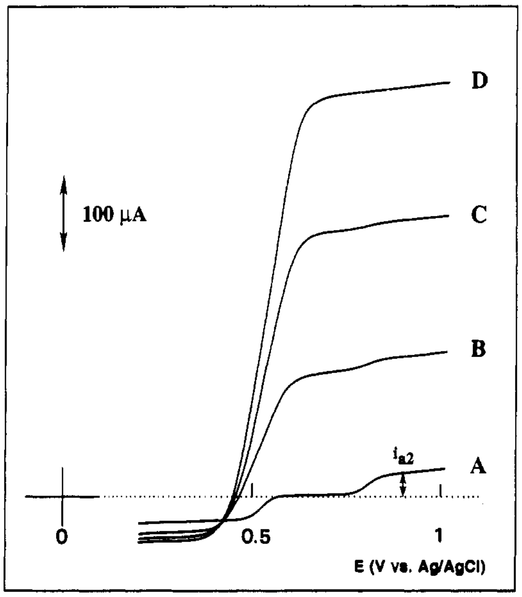

Figure 6. Rotating disk current-potential curves for a 2 mM solution of $V(salen)^{2+}$ to which VO(salen) was added. The quantities of VO(salen) added (mmol/L) were (A) 0, (B) 5, (C) 10, and (D) 15. Electrode rotation rate = 100 rpm. A 4-mm-diamter platinum electrode was used. Other conditions were as in Figure 1.

converted to Ph_3COCPh_3 is not expected on the basis of reaction 4 and needs to be explained.

The results of adding VO(salen) to a solution of $V(salen)^{2+}$ in the absence of acid is shown in the rotating disk voltammograms in Figure 6. The initial anodic plateau current, i_{a2}, decreases continuously as VO(salen) is added until the anodic wave near 0.8 V is essentially eliminated. It is evident that the deoxygenated complex $V(salen)^{2+}$ is consumed in a reaction with VO(salen). The formation of an oxo-bridged dimer as in reaction 5 seemed a likely possibility.[14] It was possible to prepare and isolate the

$$V(salen)^{2+} + VO(salen) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [(salen)VOV(salen)]^{2+};\ K \quad (5)$$

suspected dimer from a different solvent as described in the Experimental Section. A sample of the isolated dimer dissolved in anhydrous acetonitrile produced the electrochemical responses shown in Figure 7. Two anodic waves and one cathodic wave are present. The anodic wave near 0.8 V matches that obtained in pure solutions of $V(salen)^{2+}$ which suggests that reaction 5 constitutes a reversible equilibrium and that solutions prepared from the dimeric $[(salen)VOV(salen)]^{2+}$ complex also contain VO(salen) and $V(salen)^{2+}$. A striking feature in the voltammogram in Figure 7B is the presence of the composite anodic–cathodic wave. There is no reason to expect the oxidation of $[(salen)VOV(salen)]^{2+}$ to $[(salen)VOV(salen)]^{3+}$ and its reduction to $[(salen)VOV(salen)]^{+}$ to occur at the same potential so as to produce a composite wave. However, the products of the dissociation of the dimer, VO(salen) and $V(salen)^{2+}$, are oxidized and reduced, respectively, at very nearly the same potential (compare Figure 7B with Figure 1B, curve 1, and Figure 2B) so that the simultaneous presence of both of these complexes could give rise to the observed composite wave in Figure 7B.

Kinetics and Equilibrium Constant of Reaction 5. The visible spectra of solutions containing VO(salen), $V(salen)^{2+}$ and $[(salen)VOV(salen)]^{2+}$ were utilized to evaluate both the equilibrium constant of reaction 5 and the rate at which the equilibrium is established. The addition of $V(salen)^{2+}$ to a solution of VO(salen) results in a new absorption band at 567 nm with an intensity much larger than the absorption of either of the mononuclear complexes. For example, in Figure 8A are shown spectra of the two mononuclear complexes and of the dimer. The intense band at 567 nm may arise from an intramolecular charge transfer transition involving the two metal centers. The measured molar

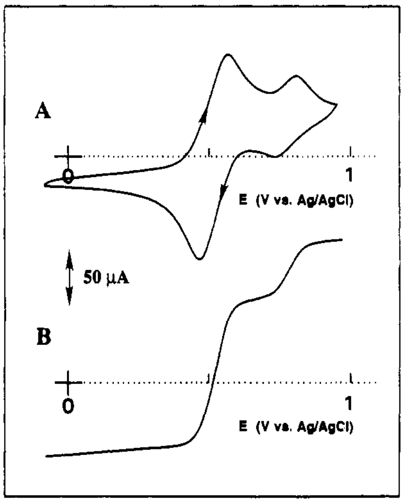

Figure 7. (A) Cyclic voltammogram and (B) rotating disk current-potential curve for a solution prepared by dissolving 2 mmol/L of $[(salen)VOV(salen)](BF_4)_2$ in anhydrous acetonitrile. Other conditions were as in Figure 1.

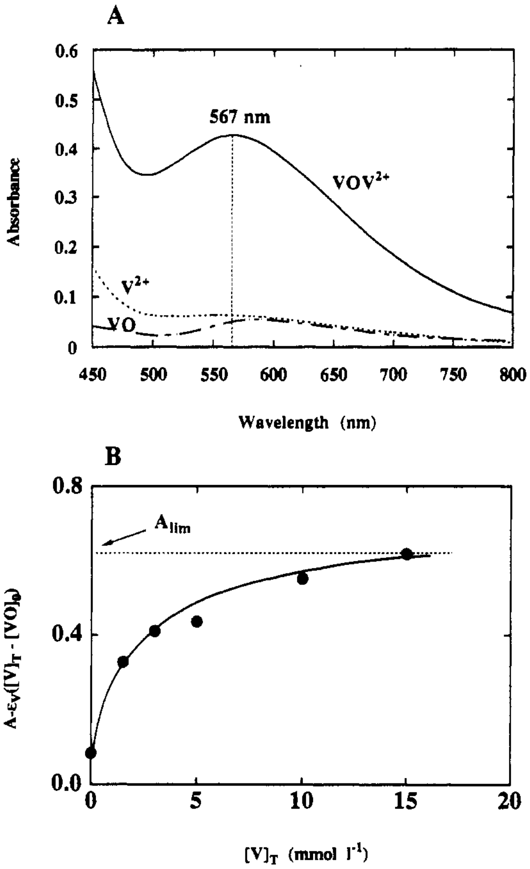

Figure 8. (A) Visible absorption spectra of 2 mM VO(salen) = VO, 2 mM $V(salen)^{2+} = V^{2+}$ and $[(salen)VOV(salen)]^{2+} = VOV^{2+}$ in anhydrous CH_3CN. The spectrum for VOV^{2+} was recorded in a solution prepared by dissolving 2 mmol/L of $[(salen)VOV(salen)](BF_4)_2$. It represents the equilibrium mixture of the three complexes involved in reaction 5. The optical path length was 0.2 cm. (B) Absorption due to $[(salen)VOV(salen)]^{2+}$ in a solution of 1.5 mM VO(salen) to which increasing quantities of $V(salen)^{2+}$ were added.

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[14] The formation of polynuclear complexes which contain a linear vanadium–oxygen chain by the reaction of VO(salen) with trityl cation have been reported by Hills et al. (a) Hills, A.; Hughes, D. L.; Leigh, G. J.; Sanders, J. R. *J. Chem. Soc., Chem. Commun.* **1991**, 827. (b) Hills, A.; Hughes, D. L.; Leigh, G. J.; Sanders, J. R. *J. Chem. Soc., Dalton Trans.* **1991**, 61.

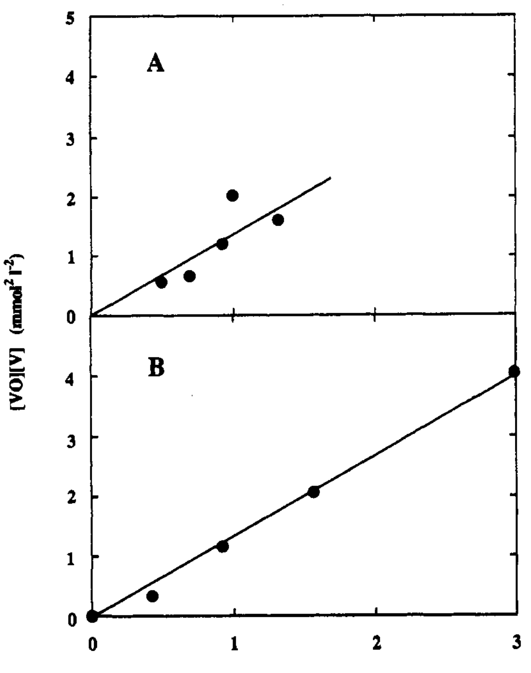

Figure 9. (A) Plot of [VO(salen)][V(salen)$^{2+}$] vs [(salen)VOV(salen)$^{2+}$] using the concentrations calculated from the data in Figure 8B and the molar absorptivities listed in Table 1. (B) Corresponding plot obtained from plateau currents at rotating disk electrodes in solutions prepared by dissolving [(salen)VOV(salen)](BF$_4$)$_2$ in CH$_3$CN (see text).

absorptivities of the three complexes at 567 nm are listed in Table 1. The value of the molar absorptivities of the dimeric complex, ϵ_{VOV}, was determined from the absorption of a solution of VO(salen) to which increasing quantities of V(salen)$^{2+}$ were added(Figure 8B). In the presence of a sufficient excess of V(salen)$^{2+}$, subtraction of the absorption calculated for the excess V(salen)$^{2+}$ from the measured absorption, produced an essentially constant absorption, A_{lim}, from which ϵ_{VOV} was calculated, $\epsilon_{VOV} = A_{lim}/[VO]_0 l$, where $[VO]_0$ is the initial concentration of VO(salen) complex and l is the optical path length. With values of the three molar absorptivities in hand the equilibrium concentrations of each complex in the mixtures employed to obtain Figure 8B were calculated.[15] The resulting values were used to prepare the plot in Figure 9A which is approximately linear with a slope corresponding to the reciprocal of the equilibrium constant for reaction 5, K^{-1} = 1.4 mM. The measurements were repeated with a solution of V(salen)$^{2+}$ to which increasing quantities of VO(salen) were added, and essentially the same results were obtained.

The relatively small value of the equilibrium constant for reaction 5, K = 0.7 mM^{-1}, indicates that the dimeric complex is substantially dissociated in acetonitrile solutions. This property of the dimer is the reason that its preparation and isolation (see Experimental Section) were carried out in dichloromethane instead of acetonitrile because it is much less dissociated in the less polar solvent. The preparation also required that Ph$_3$C$^+$ be used as the deoxygenating reagent; no other acids proved as effective in dichloromethane.

The rate at which equilibrium 5 is established is important in regard to the electrochemical experiments because separate waves for the individual complexes involved in the equilibrium are not expected unless the time required for establishment of the equilibrium is long compared with the time required for the reactants to be transported across the diffusion layer at the electrode surface. The rate of formation of the [(salen)VOV(salen)]$^{2+}$ dimer when VO(salen) was added to a solution of V(salen)$^{2+}$ was therefore measured spectrophotometrically by monitoring the absorbance of the mixtures at 567 nm as a function of time. A typical absorbance time trace is shown in Figure 10A and the appropriate kinetic plot for the approach of a reversible reaction to equilibrium with equal initial concentrations of the reactants is shown in Figure 10B.[16] The second-order rate constant obtained from the slope of the plot in Figure 10B is 0.36 mM^{-1} min^{-1}, which means that with concentrations in the millimolar range a few minutes are required for reaction 5 to attain equilibrium. It follows that the electrochemical responses shown in Figures 1, 5, 6, and 7 represent snapshots of the species present in the solution uninfluenced by the slow response of equilibrium 5 to electrochemically induced concentration changes near the electrode surface.

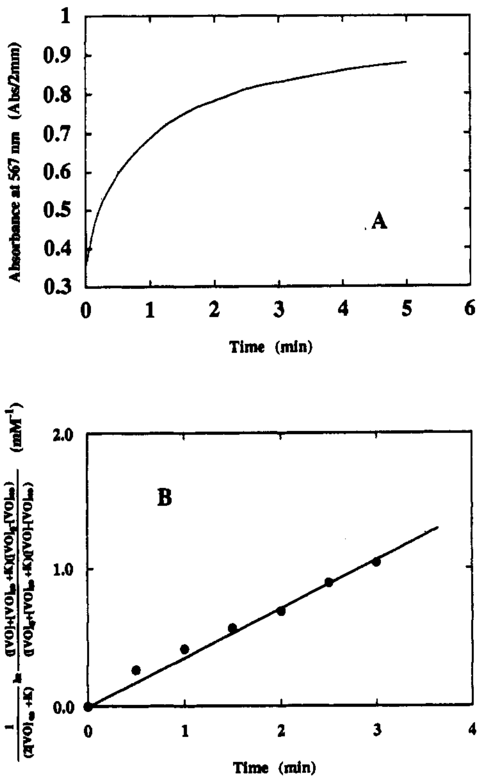

Figure 10. (A) Absorbance at 567 nm as a function of time for a solution initially containing 1.5 mM VO(salen) and 1.5 mM V(salen)$^{2+}$ in anhydrous CH$_3$CN at 25 °C. The optical path length was 0.2 cm. (B) Kinetic plot of the data from part A using the format suggested in ref 15. The equilibrium constant, K, in the ordinate was taken as 0.7 mM^{-1} on the basis of Figure 9.

Electrochemical Responses in Equilibrated Solutions Containing [(salen)VOV(salen)]$^{2+}$. In the earlier discussion of the rotating disk voltammogram shown as curve 2 in Figure 1B, it was noted that the magnitudes of the plateau currents for the three waves were inconsistent with the presence of only VO(salen) and V(salen)$^{2+}$. Having established the existence of equilibrium 5 in such solutions and its slow response to perturbations in the concentrations of the complexes, it was of interest to determine if the magnitudes of the plateau currents in voltammograms like that of curve 2 in Figure 1B could be understood. The equilibrium constant of 0.7 mM^{-1} obtained for reaction 5 means that 56% of the [(salen)VOV(salen)]$^{2+}$ dimer (hereafter VOV^{2+}) is dissociated into V(salen)$^{2+}$ and VO(salen) in an initially 2 mM solution of VOV^{2+}. The electrochemical responses obtained in such solutions are therefore a mixture of contributions from the three complexes present which complicates the analysis of current potential curves.

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(15) $[VO] = \{A - \epsilon_V([V]_0 - [VO]_0) - \epsilon_{VOV}[VO]_0\}(\epsilon_{VO} + \epsilon_V - \epsilon_{VOV})^{-1}$; $[V] = [V]_0 + [VO] - [VO]_0$; $[VOV] = [VO]_0 - [VO]$. See Table 1 for the abbreviations used for the complexes.

(16) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill Book Co.: New York, 1981; Chapter 3.

However, the situation simplifies if excess VO(salen) is added to solutions of VOV^{2+} to suppress its dissociation. For example, the extent of dissociation of the dimer is decreased from 56% to 6.5% if 20 mM VO(salen) is added to 2 mM VOV^{2+}. In the presence of such excesses of VO(salen) the second anodic wave of curve 1 in Figure 1B is nearly eliminated (Figure 6) because so little $V(salen)^{2+}$ is formed. However, the prominent cathodic wave which is present in the absence of VO(salen) (Figure 6) remains, although its magnitude increases somewhat (because the diffusion coefficient of VOV^{2+} is larger than that of $V(salen)^{2+}$ (Table 1)). This cathodic wave is believed to arise from the one-electron reduction of the $[V^{IV}OV^{IV}]^{2+}$ dimer to a mixed-valent $[V^{III}OV^{IV}]^{+}$ complex accompanied by the reduction of whatever $V(salen)^{2+}$ is still present to $V(salen)^{+}$. That the one-electron reduction of the $[V^{IV}OV^{IV}]^{2+}$ dimer occurs at potentials much less negative than are required for the reduction of VO(salen) is somewhat surprising, but the electrochemical data are reasonably compelling. The potentials where the reductions of $[V^{IV}OV^{IV}]^{2+}$ and $V(salen)^{2+}$ occur must be very similar because, in the absence of excess VO(salen), solutions of $[V^{IV}OV^{IV}]^{2+}$ which contain substantial quantities of both the dimer and $V(salen)^{2+}$, exhibit only a single reduction wave (Figure 7). The coincidence of the two reduction potentials could be explained if the dimeric complex were, in fact, not directly reducible at the electrode surface but required mediation by the $V(salen)^{2+/+}$ couple which is known to undergo facile electron transfer at the electrode. However, it is not obvious why the dimer should resist direct electroreduction.

In the presence of excess VO(salen) the dissociation of the dimer is suppressed and the magnitude of i_c provides an estimate of the diffusion coefficient of the VOV^{2+} dimer. The value obtained from the slope of a linear Levich plot of i_c vs $\omega^{1/2}$ in a solution containing 20 mM VO(salen) and 2 mM dimer was 9.2×10^{-6} cm^2 s^{-1}. This value is somewhat smaller than those obtained for the VO(salen) and $VO(salen)^{+}$ complexes (Table 1) as expected for a larger, more highly charged diffusant.

If the dissociation of the VOV^{2+} dimer is repressed by the addition of an excess of $V(salen)^{2+}$ instead of VO(salen), the first anodic wave near 0.5 V obtained in the solution of VOV^{2+} is not eliminated, as would have been expected if only the VO(salen) complex produced by the dissociation of VOV^{2+} were being oxidized at the potential. The behavior indicates that the undissociated VOV^{2+} dimer is also oxidizable in a one-electron step.

$$[V^{IV}OV^{IV}]^{2+} - e^- \rightleftharpoons [V^{V}OV^{IV}]^{3+} \qquad (6)$$

Half-reaction 6 proceeds at potentials very close to that where VO(salen) is oxidized so that separate waves are not observed for the oxidations of VO(salen) and the $[V^{IV}OV^{IV}]^{2+}$ dimer in solutions containing both species.

The three plateau currents obtained at a rotating disk electrode in solutions of VOV^{2+} provided a second means for estimating the equilibrium constant for reaction 5. The procedure was the following: The difference between i_c and i_{a2} in solutions of VOV^{2+} is proportional to the concentration of undissociated VOV^{2+} and i_{a2} provides a direct measure of the concentration of $V(salen)^{2+}$ (which will be equal to the concentration of VO(salen) in solutions prepared by dissolving VOV^{2+} in acetonitrile (Figure 7)). The concentrations of VOV and $V(salen)^{2+}$ (=VO(salen)) were evaluated for several total vanadium concentrations from the measured plateau currents using the diffusion coefficients listed in Table 1. (It was confirmed that Levich plots[11] for both i_{a2} and $i_c - i_{a2}$ were linear for electrode rotation rates between 100 and 1600 rpm, thus assuring that the measured currents were controlled only by the diffusion of the complexes.) The resulting data were used to prepare the plot shown in Figure 9B. The slope of the straight line corresponds to $K = 0.71$ mM^{-1} which is in good agreement with the value obtained in Figure 9A on the basis of the spectroscopic data.

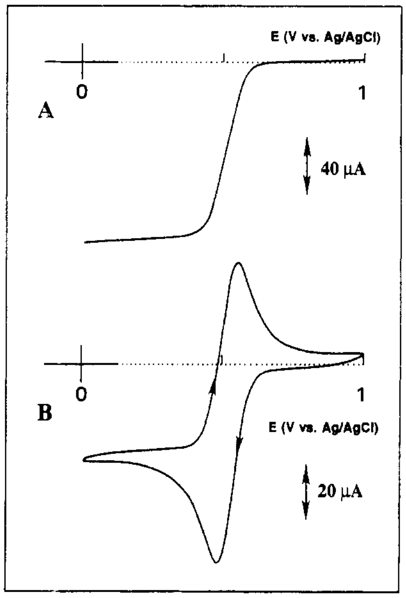

Figure 11. (A) Rotating disk current–potential curve for a 1 mM solution of $[(salen)VOV(salen)](BF_4)_2$ following controlled potential oxidation at 0.7 V which consumed one electron per molecule of dimer. A 4-mm-diameter platinum electrode was used. Electrode rotation rate = 500 rpm. Other conditions as in Figure 1. (B) Cyclic voltammogram for the solution from part A.

Controlled Potential Electrolyses of VOV^{2+}. Added support for the interpretation we have proposed for the electrochemical behavior of VOV^{2+} was provided by exhaustive electrolyses of solutions of the dimer. Oxidation of the dimer at 0.7 V at a carbon felt electrode consumed one electron per mole of dimer and the resulting solution exhibited a single reduction wave at 0.54 V at the rotating disk electrode (Figure 11A). The anodic wave at 0.8 V corresponding to the oxidation of $V(salen)^{2+}$, which was present in the original solution (Figure 7B), was not present in the oxidized solution despite the fact that the oxidation had been carried out at a potential (0.7 V) less positive than that required to oxidize $V(salen)^{2+}$. The $V(salen)^{2+}$ and VO(salen) present in the initial solution of VOV^{2+} evidently recombined during the course of the electrolysis (0.5 to 1 hour) so that the net effect of the electrolysis was the conversion of VOV^{2+} to VOV^{3+}. A cyclic voltammogram of the oxidized solution contained a single, reversible couple with peak currents corresponding to two electrons per dimeric reactant (Figure 11B). The lack of any evidence for the presence of $V(salen)^{2+}$ in the oxidized solution indicated that the oxidized dimer, VOV^{3+}, is much less dissociated than is VOV^{2+}. The magnitude of the single cathodic plateau current measured with the oxidized solution (Figure 11A) corresponded to the two-electron reduction of a reactant having a diffusion coefficient of 9×10^{-6} cm^2 s^{-1}. Thus, the VOV^{3+} complex is reduced directly to VOV^{+} in a single step.

The VOV^{2+} complex was also subjected to controlled potential *reduction* at 0.4 V. One electron per mole of complex was consumed during the electrolysis as expected for quantitative reduction to VOV^{+}. However, rotating disk voltammograms of the reduced solution contained two oxidation waves at 0.5 and 0.8 V. The latter wave corresponded to the oxidation of $V(salen)^{2+}$ and the sum of the plateau currents for the two waves amounted to one electron per vanadium center (i.e., two electrons per original dimer). The behavior was consistent with the first anodic wave's corresponding to the combined oxidations of VOV^{+} to VOV^{3+}, VO(salen) to $VO(salen)^{+}$ and $V(salen)^{+}$ to $V(salen)^{2+}$ all at essentially the same potential, followed by the oxidation of $V(salen)^{2+}$ to $V(salen)^{3+}$ at 0.8 V. Use of the plateau currents in the way described for the VOV^{2+} complex to estimate an equilibrium constant for the dissociation of the VOV^{+} dimer led to a value of ca. 10 mM which is larger than the value obtained for the VOV^{2+} dimer and is consistent with a weakening of the VOV bond as the oxidation states of the oxo-bridged metal centers are decreased.

Comparison with Previous Results. The previous study of Bonadies et al.[6] involved the addition of $HClO_4$ (presumably the commercially available 60% aqueous solution) to solutions of VO(salen) in acetonitrile. Rotating disk voltammograms similar to those shown in Figure 1B and 1C were obtained upon the addition of one or two moles of protons per mole of VO(salen). The voltammetric responses were explained in terms of proton-induced disproportionation of VO(salen). However, for the reasons given earlier, we believe that deoxygenation rather than disproportionation provides a satisfactory account of the behavior observed in anhydrous acetonitrile. With less than 2 mol of acid per mole of VO(salen), partial deoxygenation is followed by dimerization (reaction 5). In the presence of H_2O it seems likely that more than 2 equiv of acid would be required to drive reaction 4 to completion. The resulting presence of both $V(salen)^{2+}$ and VO(salen) in "wet" solutions containing 2 equiv of $HClO_4$ would result in the formation of the $(salen)VOV(salen)^{2+}$ dimer and would account for the presence of an intense band at 567 nm in the optical spectrum in ref 6. The same band was obtained in the present study by mixing VO(salen) with $V(salen)^{2+}$. The band disappears in the presence of 2 equiv or more of anhydrous protons.

In the previous study,[6] it was also reported that the EPR signal from VO(salen) was eliminated by the addition of $HClO_4$ which was taken as evidence that diamagnetic V(V) was being formed in a disproportionation reaction. However, when anhydrous acids such as CF_3SO_3H or $Ph_3C(BF_4)$ were added to solutions of VO(salen) in the present experiments, the ESR signal from the V(IV) center was changed but not eliminated (Figure 3). The signal obtained matched that obtained in the absence of acid when independently prepared samples of $[V(salen)](BF_4)_2$ were dissolved in anhydrous acetonitrile (Figure 3D). Addition of H_2O to such solutions caused the intensity of the ESR response to diminish and it seems possible that the greater quantities of H_2O in the solutions examined by Bonadies et al.[6] may have been responsible for the disappearance of the ESR response. Thus, the experimental observations of the present study and those in ref 6 are actually more similar than they may at first appear when the effects produced by the presence of water are taken into account.

In both the present and the previous study the autoxidation of VO(salen) required the presence of acid. The oxidation proceeds readily even when only 1 mol of acid per mole of VO(salen) is present which implicates the VOV^{2+} dimer as a likely reactive intermediate. The reversible two-electron redox chemistry exhibited by the $VOV^{3+/+}$ couple (Figure 11B) offers an attractive possibility for coupling the two-electron reduction of O_2 to two-electron oxidations of a variety of organic molecules. Attempts to accomplish such a coupling is the object of continuing experiments.

Table 2. Formal Potentials for Redox Couples Examined in This Study[a]

redox couple	E^f, V vs Ag/AgCl[b]
$VO(salen)^{+/0}$	0.55
$VO(salen)^{0/-}$	*c*
$V(salen)^{3+/2+}$	0.80
$V(salen)^{2+/+}$	0.53
$[(salen)VOV(salen)]^{3+/+}$	0.54

[a] Measurments made in anhydrous CH_3CN containing 0.1 M tetrabutylammonium tetrafluoroborate. [b] The formal potential of the ferrocenium/ferrocene couple was 0.470 V vs this reference electrode. [c] Irreversible reduction observed near −1.6 V accompanied by decomposition of the complex.

Conclusions

The combination of electrochemical and spectral measurements we have described has exposed additional features of the coordination and redox chemistry of the complexes of the salen ligand with V(III), V(IV), and V(V) in anhydrous acetonitrile. The conversion of VO(salen) to $V(salen)^{2+}$ by reaction with H^+ or Ph_3C^+ cations in anhydrous acetonitrile is essentially quantitative. The resulting cation is oxophilic and enters into an equilibrium with VO(salen) to form $[(salen)VOV(salen)]^{2+}$. The rate of the reactions which control this equilibrium are relatively low so that typical electrochemical measurements provide snapshots of the species present without perturbing their equilibrium distribution. Most of the complexes studied exhibit reversible redox couples in a rather narrow range of potentials as summarized in Table 2.

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