

Electrochemical Properties of Vanadium(III,IV,V)–Salen Complexes in Acetonitrile. Four-Electron Reduction of O₂ by V(III)–Salen

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The coordination chemistry and electrochemistry of complexes of vanadium(III,IV,V) with salen (H₂ salen = N,N'-ethylenebis(salicylideneamine)) were reexamined in an attempt to uncover the origin of puzzling results reported in a previous study (*Inorg. Chem.* **1994**, 33, 1056). Microelectrodes were utilized to allow measurements in the absence of supporting electrolyte. The source of the puzzling results was identified and the modifications required in the previous interpretations are specified. Corrected values of formal potentials and diffusion coefficients are also given. The acid-induced disproportionation of V^{IV}O(salen), as originally proposed by Bonadies et al. (*J. Chem. Soc., Chem. Commun.* **1986**, 1218; *Inorg. Chem.* **1987**, 26, 1218), was largely supported by the present results. The equilibrium constant for this disproportionation reaction was measured. The stoichiometry and kinetics of the reaction between O₂ and the V(III)–salen complex were examined, and a possible mechanism for this four-electron reduction of O₂ is suggested.

Introduction

The redox and electrochemical behaviors of vanadium oxo complexes with the ligand salen [H₂-salen = N,N'-ethylenebis(salicylideneamine)] in acetonitrile solution were first studied by Bonadies and co-workers.¹ Abundant structural studies of these complexes have also been reported.^{2,3} Recently, additional electrochemical studies of the complexes in both acetonitrile⁴ and dichloromethane⁵ have been described. With acetonitrile as solvent, the results were interpreted by invoking an acid-induced conversion of VO(salen) to, first, an oxo-bridged dimeric complex and, with a sufficient excess of acid, to the oxo-free complex V^{IV}(salen)²⁺.⁴ The results also included the surprising observation that the formal potentials of the VO(salen)⁺⁰ and V(salen)^{2+/+} couples were almost the same.⁴

The interpretation of the electrochemical results in ref 4 differed from that of Bonadies et al.,¹ who had proposed an acid-induced disproportionation reaction of V^{IV}O(salen) without the intervention of an oxo-bridged dimeric complex. Because of the different interpretations offered for essentially the same experimental observations and the puzzling coincidence of the formal potentials given in ref 4, we decided to reexamine the electrochemistry of the vanadium–salen system in the presence of little or no supporting electrolyte to determine if ionic interactions in the nonaqueous environment might have been responsible for some of the unexplained anomalies in the previous report.⁴ Our interest was also stimulated by the indications that vanadium–salen complexes are capable of acting as catalysts for the electrochemical reduction of O₂ by four electrons in nonaqueous solvents.^{5b,c}

The new results, summarized in this report, provide what we believe to be a more satisfying account of the effect of strong acids on the chemistry and electrochemistry of the vanadium–salen system in acetonitrile as solvent. The participation of a disproportionation reaction, as originally proposed by Bonadies et al.,¹ is strongly supported by the present results, and the equilibrium constant for the disproportionation was estimated. The origin of the puzzling behavior that led Tsuchida et al.⁴ to propose an alternative interpretation is identified. In addition, the stoichiometry and kinetics of the reaction between O₂ and a V(III)–salen complex are reported, and a possible mechanism is proposed for the catalysis by the complex of the electroreduction of O₂ by four electrons in acidified acetonitrile.

Experimental Section

Materials. N,N'-Ethylenebis(salicylideneamine) (H₂-salen) and tris(acetylacetonato)vanadium(III) were obtained from Pfaltz & Bauer and Aldrich, respectively. V^{IV}O(salen) was prepared according to a published procedure⁶ and purified by recrystallization from dichloromethane–methanol. Supporting electrolytes from Fluka were of

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electrochemical grade. They were dried overnight at 75 °C in a vacuum oven. Distilled acetonitrile containing 0.001% water was supplied by EM Science and stored over 3A molecular sieves. Trifluoromethanesulfonic (triflic) acid from Sigma was received under argon and was maintained O₂-free by saturation with Ar.

[V^{III}(salen)]CF₃SO₃·2CH₃CN. V^{IV}O(salen) (0.600 mmol, 0.2 g) was dissolved in acetonitrile (75 mL). In the solution was placed a platinum gauze that had been cleaned with HNO₃ and washed thoroughly with water, acetone, and acetonitrile. The solution was purged with argon for 20 min and an equimolar quantity of CF₃SO₃H (56 μL) was slowly added to the solution under an argon atmosphere. Hydrogen was then passed through the solution until the reaction was complete [as determined by the disappearance of the wave for the reduction of V^{VO}(salen)⁺, formed by disproportionation of V^{IV}O(salen), in microelectrode voltammograms]. The solvent was removed under argon and the brownish yellow powder obtained was placed under vacuum to complete the solvent removal. Anal. Calcd for [V^{III}(salen)]CF₃SO₃·2CH₃CN: C, 45.99; H, 3.68; N, 10.22. Found: C, 45.59; H, 3.60; N, 10.32.

Apparatus and Procedures. Electrochemical measurements were carried out in conventional one- or two-compartment cells using a Bioanalytical Systems Model 100B/W electrochemical analyzer. Solutions were kept under an atmosphere of argon, which was purified by passing through a gas scrubber (Oxiclear, Aldrich) and two columns filled with molecular sieves. A 10 μm diameter carbon microelectrode or a 5 mm diameter glassy carbon disk were used as the working electrodes in voltammetric experiments. The electrodes were polished with 0.3 μm and 0.05 μm alumina pastes before use. A porous glassy carbon working electrode was used for bulk electrolyses. The auxiliary electrode was a platinum wire or foil. The reference electrode was Ag/AgCl in CH₃CN saturated with NaCl. All potentials are quoted with respect to this electrode. The half-wave potentials of the ferrocenium/ferrocene couple measured from microelectrode voltammograms recorded in pure acetonitrile and in a 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) solution in acetonitrile were 0.47 and 0.44 V, respectively, vs this Ag/AgCl reference electrode.

The rate of the reaction between V^{III}(salen)⁺ and O₂ in acetonitrile solution at 24 ± 0.5 °C was measured by following the formation of the product, V^{VO}(salen)⁺, with a Hewlett-Packard 8452A diode-array spectrophotometer. IR spectra were obtained with a Perkin-Elmer 1600 FT-IR spectrophotometer and a cell with CaF₂ windows separated by 1 mm. Background spectra were measured with pure acetonitrile. ⁵¹V NMR spectra were obtained on a Varian Inova 500 spectrometer operating at 131.47 MHz with neat VOCl₃ as an external reference. EPR spectra were recorded on a Varian E-line spectrometer operating at X-band. A cylindrical quartz cell with a diameter of 2 mm was used as the sample tube.

Results

Acid-Induced Disproportionation of V^{IV}O(salen). The reaction of V^{IV}O(salen) with triflic acid (CF₃SO₃H) in anhydrous acetonitrile containing no other electrolyte is readily monitored by means of steady-state voltammetry using a carbon microelectrode.⁷ Curve 1 in Figure 1 is the response obtained from V^{IV}O(salen) before the addition of acid. The single oxidation wave, corresponding to half-reaction 1, matches that reported in previous studies in the presence of supporting electrolyte.^{1,4}



Addition of 1 mol of CF₃SO₃H per mol of V^{IV}O(salen) produced the separated oxidation and reduction waves shown in curve 2. This behavior differs significantly from that reported in ref 4, where tetrabutylammoniumtetrafluoroborate (TBABF₄) was employed as a supporting electrolyte. In that study, the addition of an equimolar quantity of acid produced a composite

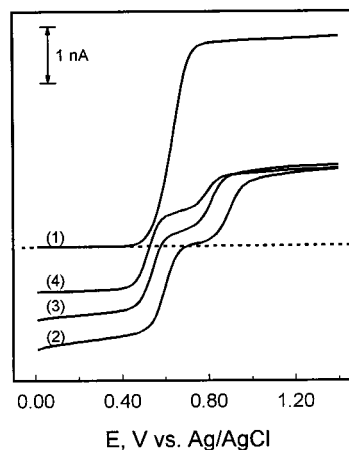
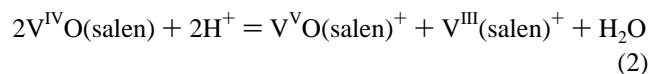


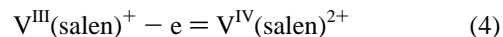
Figure 1. Steady-state voltammetry of a 1.0 mM solution of V^{IV}O(salen) in CH₃CN recorded with a carbon microelectrode scanned at 10 mV s⁻¹. For this and the subsequent figures, the position of zero current is shown by the dotted line. Supporting electrolyte: (1) none, (2) 1 mM CF₃SO₃H, (3) 1 mM CF₃SO₃H + 20 mM TBABF₄, (4) 1 mM CF₃SO₃H + 60 mM TBABF₄.

anodic/cathodic wave followed by an anodic wave at more positive potentials. Curve 3 in Figure 1 shows the voltammetric response obtained in the presence of TBABF₄. As the concentration of TBABF₄ is increased, the cathodic plateau currents corresponding to the reduction of V^{VO}(salen)⁺ become much smaller and the magnitude of the second anodic plateau current is also diminished (curve 4 in Figure 1). The anomalous behavior provoked by the presence of TBABF₄ originates in the BF₄⁻ anion. With supporting electrolytes consisting of 0.1 M TBAPF₆, TBAClO₄ or TBACF₃SO₃, voltammetric responses similar to curve 2 in Figure 1 are obtained.

The separated anodic and cathodic waves in curve 2 of Figure 1 are consistent with an acid-induced disproportionation of V^{IV}O(salen) according to reaction 2



with the cathodic wave at 0.65 V and the anodic wave at 0.9 V assigned to half-reactions 3 and 4, respectively.



The presence of vanadium(V) in acidified solutions of V^{IV}O(salen) was confirmed by recording a ⁵¹V NMR spectrum which contained a peak at -598 ppm (Figure S1A in Supporting Information) assignable to the diamagnetic V^{VO}(salen)⁺ complex.⁸ In addition, the eight-line ESR spectrum exhibited by pure solutions of V^{IV}O(salen) disappeared in the presence of an equimolar quantity of acid (Figure S1B), as expected if reaction 2 proceeded essentially to completion.

Equilibrium Constant for the Disproportionation Reaction. If less than equivalent quantities of CF₃SO₃H are added to solutions of V^{IV}O(salen) in anhydrous acetonitrile, reaction 2 still proceeds too extensively to allow its equilibrium constant to be measured. However, in the presence of excess H₂O, the

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Table 1. Evaluation of the Equilibrium Constant for Reaction 2 from the Plateau Currents of the Curves in Figure 2^a

equiv of HClO ₄ added	[V ^{IV} O(salen)] ^b , mM	[V ^{VO} (salen)] ⁺ ; ^c , mM	[V ^{III} (salen)] ⁺ ; ^d , mM	[H ⁺] ^e , mM	10 ^{-6f} K ₂ , M ⁻¹
0	1.0	0	0	0	
0.15	0.87	0.065	0.065	0.02	1.4
0.30	0.74	0.13	0.13	0.04	1.9
0.45	0.63	0.18	0.18	0.08	1.3
0.60	0.52	0.24	0.24	0.12	1.5
0.75	0.41	0.29	0.29	0.17	1.7
0.90	0.33	0.34	0.34	0.22	2.1
					av (1.6 ± 0.3)

^a Steady-state current–potential curves were recorded at a carbon microelectrode in CH₃CN containing 0.1 M H₂O, 0.1 TBAClO₄, and (initially) 1 mM V^{IV}O(salen). ^b Calculated as 1.0 – 2[V^{VO}(salen)]⁺. ^c Evaluated from the cathodic plateau currents of the curves in Figure 2. ^d Taken as equal to [V^{VO}(salen)]⁺. ^e Calculated from the difference between the amount of HClO₄ added (assumed to be totally dissociated (12)) and [V^{VO}(salen)]⁺ using the stoichiometry of reaction 2. ^f K₂ ≡ [V^{VO}(salen)]⁺[V^{III}(salen)]⁺ [H₂O]/[V^{IV}O(salen)]²[H⁺]².

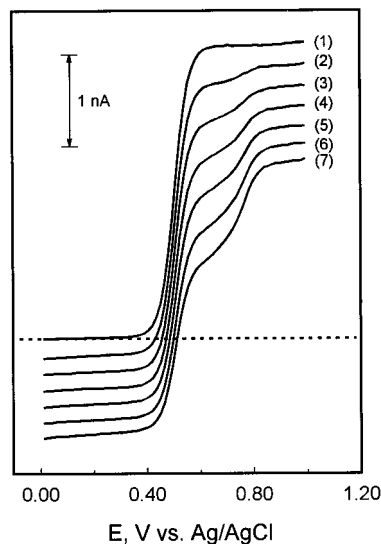


Figure 2. Steady-state voltammograms recorded with a carbon microelectrode in an initially 1.0 mM solution of V^{IV}O(salen) in CH₃CN also containing 0.1 M TBAClO₄ + 0.1 M H₂O. Aliquots of 70% HClO₄ were added to the solution in quantities corresponding to (1) 0, (2) 0.15, (3) 0.30, (4) 0.45, (5) 0.60, (6) 0.76, (7) 0.40 mol of HClO₄ per mol of V^{IV}O(salen). Other conditions as in Figure 1.

reaction comes to equilibrium with substantial quantities of the acid remaining, which permits the equilibrium constant to be estimated. Shown in Figure 2 is a set of current–potential curves recorded after increasing quantities of CF₃SO₃H were added to a solution of V^{IV}O(salen) in CH₃CN containing 0.1 M H₂O. The composite cathodic/anodic wave and the separate anodic wave near 0.8 V reflect the simultaneous presence in the solution of all three of the complexes involved in reaction 2. The well-formed cathodic plateau current measured the concentration of V^{VO}(salen)⁺ in each solution which was used to calculate the corresponding equilibrium concentrations of the other reactants in the equilibrium of reaction 2. The various concentrations were combined to obtain values for the equilibrium constant as summarized in Table 1. The reasonably constant value obtained for K₂ supports the proposition that reaction 2 reliably describes the acid-induced disproportionation of V^{IV}O(salen).

Electrochemical Behavior of V^{VO}(salen)⁺. The disproportionation of V^{IV}O(salen) in acidic acetonitrile would be expected to enhance the cathodic plateau current for the reduction of V^{VO}(salen)⁺ in the presence of acid. Shown in Figure 3 is a set of steady-state voltammograms that demonstrate the expected effect. In the absence of acid (curve 1 in Figure 3) a one-electron reduction according to half-reaction 3 proceeds. However, in the presence of acid, larger cathodic plateau currents result

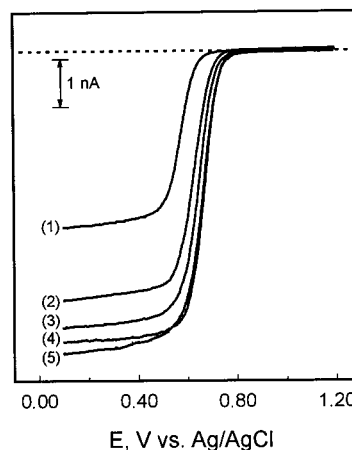
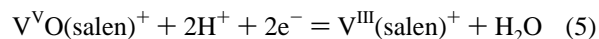


Figure 3. Steady-state voltammetry of a 1.0 mM solution of V^{VO}(salen)⁺ prepared by saturating a mixture of 1 mM V^{IV}O(salen) and 1 mM CF₃SO₃H with O₂ for 30 min followed by removal of the O₂ with Ar. Supporting electrolyte: (1) 0, (2) 1, (3) 2, (4) 4, (5) 8 mM CF₃SO₃H. Other conditions as in Figure 1.

(curves 2–5). The reason is that half-reaction 3 is followed by reaction 2, which produces additional V^{VO}(salen)⁺ that again undergoes half-reaction 3, etc.

As expected, the rate of reaction 2 increases with the concentration of acid so the plateau current increases until it reaches a value close to the diffusion-controlled, two-electron reduction of V^{VO}(salen)⁺ according to the stoichiometry given in half-reaction 5.



The positive shift in the half-wave potentials of the curves in Figure 3 as the concentration of acid is increased is also a reflection of the increase in the rate of reaction 2, which diminishes the concentration of V^{IV}O(salen) at the electrode surface.

Electrolysis at 0.4 V of solutions of V^{VO}(salen)⁺ like the one used to record curve 2 in Figure 3 consumed two electrons per molecule of V^{VO}(salen)⁺, even though the plateau current of curve 2 corresponds to fewer than two electrons. The reason is that the rate of reaction 2 was ample for the quantitative disproportionation of all V^{IV}O(salen) produced during the 30–40 min required for the electrolysis.

Additional evidence of the occurrence of reaction 2 is provided by the cyclic voltammograms shown in Figure 4. In the absence of acid (Figure 4A), only a single reversible response, corresponding to the VO(salen)⁺⁰ couple, is observed. However, in the presence of acid (Figure 4B) the occurrence of reaction 2 produces a second reversible response near 0.8 V

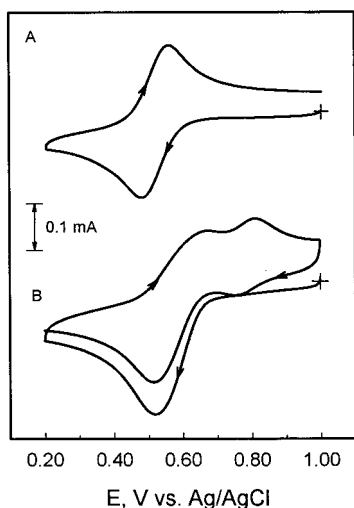
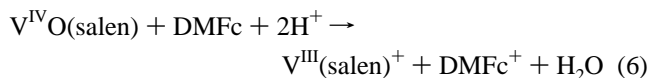


Figure 4. Cyclic voltammety of a 1.0 mM solution of $V^{VO}(\text{salen})^+$ (prepared by electro-oxidation of $V^{IV}O(\text{salen})$). Before (A) and after (B) the solution was made 2 mM in $\text{CF}_3\text{SO}_3\text{H}$; supporting electrolyte, 0.1 M TBAPF_6 ; scan rate, 250 mV s^{-1} ; electrode, 5 mm diameter glassy carbon.

that corresponds to the $V(\text{salen})^{2+/+}$ couple. This response can be detected at scan rates as high as $\sim 2.5 \text{ V s}^{-1}$, so under the experimental conditions employed, the disproportionation of $V^{IV}O(\text{salen})$ according to reaction 2 occurs within a few tenths of a second.

Quantitative Conversion of $V^{IV}O(\text{salen})$ to $V^{III}(\text{salen})^+$. In the absence of acid, $V^{IV}O(\text{salen})$ exhibits no reductive electrochemistry at potentials as negative as -1.6 V , so its direct reduction to the V(III) oxidation state is very slow. However, the reduction of $V^{IV}O(\text{salen})^+$ (generated via reaction 2) to $V^{IV}O(\text{salen})$ followed by the recurrence of reaction 2 provides a pathway for the quantitative electrolytic conversion of $V^{IV}O(\text{salen})$ to $V^{III}(\text{salen})^+$. To avoid the presence of supporting electrolytes required in electrolytic reductions, chemical reductants were examined. Decamethylferrocene (DMFc) proved to be suitable. Shown in Figure 5A, curve 1, is the steady-state voltammogram obtained with a solution that contained 1 mM $V^{IV}O(\text{salen})$ and 1 mM DMFc. The anodic wave near 0 V corresponds to the oxidation of DMFc to DMFc^+ and that at 0.65 V to the oxidation of $V^{IV}O(\text{salen})$. (The larger plateau current for the first wave reflects the larger diffusion coefficient of DMFc.) The addition of 2 mmol/L of $\text{CF}_3\text{SO}_3\text{H}$ to the solution used to record curve 1 caused the steady-state voltammogram to change to the one shown in curve 2. The wave for the oxidation of $V^{IV}O(\text{salen})$ has been replaced by the wave near 0.9 V corresponding to the oxidation of $V^{III}(\text{salen})^+$, and the DMFc has been oxidized to DMFc^+ , which is responsible for the cathodic wave near 0 V. Thus, the addition of 2 equiv of acid caused reaction 6 to proceed quantitatively.



The loss of the vanadium–oxo bond as a result of reaction 6 was confirmed by comparison of the IR spectra of two solutions similar to those in Figure 5A. As shown in Figure 5B, a band at 985 cm^{-1} , present in the original solution of $V^{IV}O(\text{salen})$ and originating in the $\text{V}=\text{O}$ stretching mode,⁹ is absent after the addition of acid caused reaction 6 to occur.

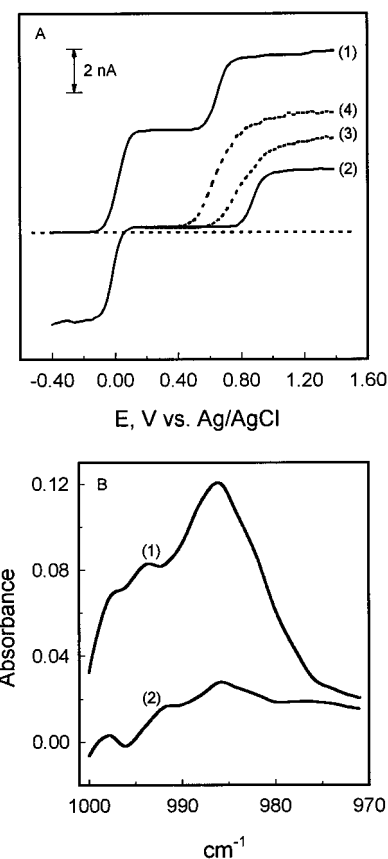


Figure 5. (A) Steady-state voltammety in a solution containing 1.0 mM $V^{IV}O(\text{salen})$ and 1 mM DMFc before (1) and after (2) the solution was made 2 mM in $\text{CF}_3\text{SO}_3\text{H}$. The dotted curves are the responses obtained when the solution was subsequently made 0.1 M (curve 3) or 1.0 M (curve 4) in H_2O . Other conditions as in Figure 1. (B) Infrared spectra of (1) 2 mM $V^{IV}O(\text{salen})$ in CH_3CN and (2) a mixture of 2 mM $V^{IV}O(\text{salen})$, 2 mM DMFc, and 4 mM $\text{CF}_3\text{SO}_3\text{H}$.

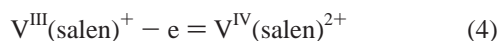
A solid sample of $V(\text{salen})[\text{CF}_3\text{SO}_3] \cdot (\text{CH}_3\text{CN})_2$, prepared by reduction of $\text{VO}(\text{salen})$ with H_2 in the presence of acid (see Experimental Section), also lacked the IR peak at 985 cm^{-1} that was present in solid samples of $V^{IV}O(\text{salen})$. Thus, the reduction of $V^{IV}O(\text{salen})$ in acidified acetonitrile produces an oxo-free complex that probably contains CH_3CN molecules as axial ligands.

Electrochemical Behavior of $V^{III}(\text{salen})^+$. The anodic wave near 0.9 V in curves 2 of Figures 1 and 5A was attributed to the oxidation of $V^{III}(\text{salen})^+$. In accord with this assignment, solutions prepared from isolated samples of $V(\text{salen})[\text{CF}_3\text{SO}_3] \cdot (\text{CH}_3\text{CN})_2$ exhibited a single anodic wave identical to those in curve 2 of Figures 1 and 5A. (As expected, the wave was unaffected by the addition of up to 0.1 M TBAPF_4 .) The magnitude of the anodic plateau current in curve 2 of Figure 5A is comparable to that for the one-electron oxidation of $V^{IV}O(\text{salen})$ in curve 1, which suggests that a one-electron oxidation of $V^{III}(\text{salen})^+$ to $V^{IV}(\text{salen})^{2+}$ is occurring. However, when a solution like the one used to record curve 2 in Figure 5A was subjected to controlled potential oxidation at 1.2 V using a large area glassy carbon electrode (after 0.1 M TBAPF_6 was added as a supporting electrolyte), two electrons were removed from each $V^{III}(\text{salen})^+$ molecule and the solution turned deep blue, the color characteristic of $V^{VO}(\text{salen})^+$. The electrolyzed solution also contained acid (presumably generated during the electrolysis) because a small quantity of $V^{IV}O(\text{salen})$ added to the electrolyzed solution disproportionated into $V^{III}(\text{salen})^+$ and $V^{VO}(\text{salen})^+$ instead of remaining as $V^{IV}O(\text{salen})$ with its

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characteristic oxidation potential. The behavior observed can be understood on the basis of the set of reactions in Scheme 1

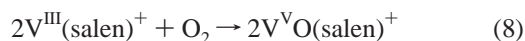
Scheme 1



The oxidation of $\text{V}^{\text{III}}(\text{salen})^+$ begins with a one-electron oxidation (half-reaction 4). The resulting oxophilic $\text{V}^{\text{IV}}(\text{salen})^{2+}$ would be expected to undergo reaction with the residual H_2O that was released during the preparation of the $\text{V}^{\text{III}}(\text{salen})^+$ solution, and the resulting $\text{V}^{\text{IV}}\text{O}(\text{salen})$ would be electro-oxidized to $\text{V}^{\text{VO}}(\text{salen})^+$ (half-reaction 1) at the positive potential (1.2 V), where the electrolysis was carried out. Thus, an overall two-electron oxidation of $\text{V}^{\text{III}}(\text{salen})^+$ is obtained. The anodic plateau current in curve 2 of Figure 5A corresponds to only a one-electron oxidation because reaction 7 proceeds too slowly to affect the plateau current in the microelectrode voltammograms that were recorded in ca. 1 min, but during the 30–40 min required for controlled potential electrolysis experiments, reaction 7 has time to occur, and two-electrons are removed from each $\text{V}^{\text{III}}(\text{salen})^+$ complex.

Additional support for Scheme 1 was obtained when increasing quantities of water were added to solutions of $\text{V}^{\text{III}}(\text{salen})^+$. The dotted curves in Figure 5A show the increases in anodic current produced by the addition of H_2O . The interpretation is that the added water caused the rate of reaction 7 (Scheme 1) to increase so that half-reaction 1 could contribute to the anodic plateau current. With 1 M H_2O the magnitude of the current had almost doubled, as expected on the basis of Scheme 1.

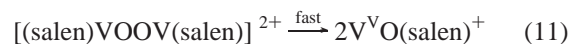
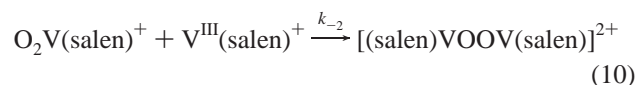
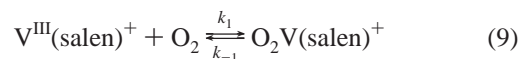
Reaction between $\text{V}^{\text{III}}(\text{salen})^+$ and O_2 . $\text{V}^{\text{III}}(\text{salen})^+$ in acetonitrile reacts with O_2 to produce $\text{V}^{\text{VO}}(\text{salen})^+$ according to reaction 8.



The stoichiometry of reaction 8 was examined by adding measured aliquots of a standard solution of $\text{V}^{\text{III}}(\text{salen})^+$ in $\text{CH}_3\text{-CN}$ to a solution containing excess O_2 in CH_3CN and measuring (either electrochemically or spectrophotometrically) the quantity of $\text{V}^{\text{VO}}(\text{salen})^+$ produced. The conversion of $\text{V}^{\text{III}}(\text{salen})^+$ to $\text{V}^{\text{VO}}(\text{salen})^+$ was quantitative. The ^{51}V NMR spectrum of the reaction solution also confirmed the production of $\text{V}^{\text{VO}}(\text{salen})^+$ (Figure S1). The possibility that H_2O_2 might have been among the products of reaction 8 was ruled out by the observation that H_2O_2 oxidizes $\text{V}^{\text{III}}(\text{salen})^+$ rapidly and quantitatively to $\text{V}^{\text{VO}}(\text{salen})^+$.

The kinetics of reaction 8 were examined spectrophotometrically by monitoring the increase in the concentration of $\text{V}^{\text{VO}}(\text{salen})^+$. Shown in Figure S2 (Supporting Information) are the absorption spectra of $\text{V}^{\text{III}}(\text{salen})^+$ and $\text{V}^{\text{VO}}(\text{salen})^+$ in acetonitrile. The absorbance at 570 nm is dominated by the oxidized complex, so the reaction was conveniently followed at this wavelength. Typical pseudo-first-order kinetic plots (with O_2 in excess) are shown in Figure S3. The linearity of the plots and the ratio of their slopes demonstrated that the reaction rate was first-order with respect to $\text{V}^{\text{III}}(\text{salen})^+$ and O_2 , respectively. A likely mechanism consistent with this behavior is given in Scheme 2

Scheme 2



Applying the steady-state approximation to $[\text{O}_2\text{V}(\text{salen})^+]$ and $[(\text{salen})\text{VOOV}(\text{salen})]^{2+}$ leads to the rate law in eq 12

$$\frac{-d[\text{V}^{\text{III}}(\text{salen})^+]}{dt} = \frac{2k_1k_2[\text{V}^{\text{III}}(\text{salen})^+]^2[\text{O}_2]}{k_{-1} + k_2[\text{V}^{\text{III}}(\text{salen})^+]} \quad (12)$$

The observed first order dependence of the rate on $[\text{V}^{\text{III}}(\text{salen})^+]$ implies that $k_{-1} \ll k_2[\text{V}^{\text{III}}(\text{salen})^+]$ so that the rate law becomes

$$\frac{-d[\text{V}^{\text{III}}(\text{salen})^+]}{dt} = 2k_1[\text{V}^{\text{III}}(\text{salen})^+][\text{O}_2] \quad (13)$$

Kinetic plots of the integrated rate law (Figure S3) correspond to a value of $0.07 \text{ M}^{-1} \text{ s}^{-1}$ for k_1 . The kinetics of reaction 8 are more complicated when larger concentrations of $\text{V}^{\text{III}}(\text{salen})^+$ are employed: Behavior consistent with Scheme 2 is observed initially but deviations occur at later times. The origin of this behavior is still under investigation.

Discussion

Examination of the behavior of $\text{V}^{\text{IV}}\text{O}(\text{salen})$ in acetonitrile in the presence of $\text{CF}_3\text{SO}_3\text{H}$, but no other supporting electrolyte, established that disproportionation induced by the added acid controls the electrochemical behavior. The interpretations proposed in the present study have elements in common with those offered in two previous reports,^{1,4} but there are also some significant differences.

Comparison with Previous Studies. The puzzling and unexpected coincidence of the formal potentials for the $\text{VO}(\text{salen})^{+/0}$ and $\text{V}(\text{salen})^{2+/+}$ couples reported by Tsuchida et al.⁴ was based on the development of a composite anodic/cathodic wave when acid was added to solutions of $\text{V}^{\text{IV}}\text{O}(\text{salen})$ containing TBABF_4 as supporting electrolyte (as in curves 3 and 4 of Figure 1). However, with anhydrous acetonitrile, no composite wave develops in the absence of supporting electrolyte (curve 2 of Figure 1) or in the presence of supporting electrolytes that do not contain BF_4^- anions. The behavioral pattern suggests that BF_4^- may exhibit significant basicity in CH_3CN . This basicity of BF_4^- was confirmed by experiments with an acid–base indicator. Following the procedures of Kolthoff et al.,^{10,11} the indicator “neutral red” was employed to estimate a $\text{p}K_a$ for HBF_4 in CH_3CN . The value obtained, $\text{p}K_a \sim 5.0$, is comparable to the value for HBr , $\text{p}K_a = 5.5$ ¹⁰ but much higher than that for HClO_4 ($\text{p}K_a = 1.6$) or $\text{CF}_3\text{SO}_3\text{H}$ ($\text{p}K_a = 2.6$).¹² Thus, BF_4^- is a considerably stronger base in CH_3CN than are ClO_4^- and CF_3SO_3^- . The basic character of BF_4^- anions in CH_3CN could cause reaction 2 to proceed only part way in the presence of stoichiometric quantities of strong acids ($\text{CF}_3\text{SO}_3\text{H}$ or HClO_4) in supporting electrolytes containing

(10) Kolthoff, I. M.; Bruckenstein, S.; Chantooni, M. K., Jr. *J. Am. Chem. Soc.* **1961**, *83*, 3927.

(11) Kolthoff, I. M.; Chantooni, M. K., Jr.; Bhowmik, S. *Anal. Chem.* **1967**, *39*, 315. (Note that the curves in Figure 1 are mislabeled.)

(12) Fujinaga, T.; Sakamoto, I. *J. Electroanal. Chem.* **1977**, *85*, 185.

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

redox couple	E^f , V vs Ag/AgCl ^b
VO(salen) ⁺⁰	0.51
V(salen) ^{2+/+}	0.78
V ^{IV} O(salen) + 2H ⁺ + e ⁻ = V ^{III} (salen) ⁺ + H ₂ O	0.88 ^c
V ^V O(salen) ⁺ + 2H ⁺ + 2e ⁻ = V ^{III} (salen) ⁺ + H ₂ O	0.70 ^c

^a The potentials apply to anhydrous CH₃CN in the presence of 0.1 M supporting electrolyte (TBAClO₄ or TBAPF₆). The values supersede those given in ref 4. ^b The potential of the ferrocenium/ferrocene couple was 0.44 V vs this reference electrode. ^c Calculated from the equilibrium constant for reaction 2 (Table 1) and E^f for VO(salen)⁺⁰.

BF₄⁻ anions. Such behavior would account for the composite cathodic/anodic wave observed by Tsuchida et al.⁴ because both V^{IV}O(salen) and V^VO(salen)⁺ (as well as V^{III}(salen)⁺) would have been present in their solutions. In acidified supporting electrolytes containing less basic ClO₄⁻, CF₃SO₃⁻, or PF₆⁻ anions, we observe only well-separated cathodic and anodic waves. It now seems clear that Tsuchida et al.⁴ were misled by the appearance of the composite cathodic/anodic wave in their experiments.

Bonadies et al.¹ reported results similar to those shown in curve 2 of Figure 1 when HClO₄ (presumably a concentrated aqueous solution) was added to solutions of V^{IV}O(salen) in acetonitrile containing 0.1 M TBAPF₆ as supporting electrolyte. An acid-induced disproportionation of the V^{IV}O(salen) was proposed, but the stoichiometry of the reaction appeared to require 2 equiv of acid for each V^{IV}O(salen) complex rather than the single equivalent of acid we found to be sufficient to cause reaction 2 to proceed quantitatively (curve 2 in Figure 1). We believe the difference can be attributed to the presence of water in solutions of HClO₄. (The commercially available 70% solution of HClO₄ contains 27.2 M H₂O.) The acidity of HClO₄ in (wet) acetonitrile is weaker than that of anhydrous CF₃SO₃H, so additional HClO₄ is required to force reaction 2 to completion. When water was added to the anhydrous CF₃SO₃H, or if the commercially available acetonitrile solvent was not subjected to a desiccating treatment before it was used, more than 1 equiv of the acid was required to cause reaction 2 to proceed quantitatively.

The results of the present reexamination of the system indicate that the acid-induced “deoxygenation” reaction proposed by Tsuchida et al.⁴ and the acid-induced disproportionation reaction proposed by Bonadies et al.¹ can be assigned to the same process, reaction 2, which goes to completion in the absence of BF₄⁻ or excess H₂O but reaches an intermediate equilibrium state in their presence unless significant excesses of acid are added. Thus, except for its stoichiometry, the disproportionation step originally proposed by Bonadies et al.¹ is fully supported by the present results.

Estimates of formal potentials and diffusion coefficients that were reported in ref 4 require correction in the light of the present results. Revised values of the potentials and diffusion coefficients are listed in Tables 2 and 3. Tsuchida et al.⁴ also proposed an important role for an oxo-bridged dimer, (salen)-VOV(salen)²⁺, in the electrochemical responses of acidified solutions of V^{IV}O(salen) in CH₃CN (0.1 M TBAPF₆). Such oxo-bridged complexes have been reported in crystalline samples by Leigh and co-workers,² but their persistence in dilute CH₃CN solutions is doubtful. For example, acidified solutions of V^{IV}O(salen) containing BF₄⁻, which exhibit a composite wave like curve 4 in Figure 1, give ESR spectra indicating the presence of only V^{IV}O(salen), not the V^{IV}(salen)²⁺ complex proposed in ref 4 to result from the dissociation of a dimeric

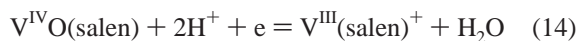
Table 3. Diffusion Coefficients for Complexes Examined in This Study^a

complex	10 ⁵ D , cm ² s ⁻¹ ^b
V ^V O(salen) ⁺	1.0
V ^{IV} O(salen)	1.2
V ^{III} (salen) ⁺	1.0

^a Calculated from plateau currents at rotating glassy carbon disk electrodes in CH₃CN containing 0.1 M TBAPF₆. ^b These values supersede those given in ref 4.

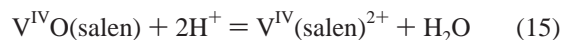
complex. The electrochemical results obtained in the present study were satisfactorily accounted for without the need to invoke the presence of stable dimeric species. The formal potentials and diffusion coefficients reported for the dimeric complexes in ref 4 should be disregarded.

The equilibrium constant obtained for the disproportionation reaction, $K_2 = 1.6 \times 10^6 \text{ M}^{-1}$ (Table 1), can be combined with the formal potential of the VO(salen)⁺⁰ couple, 0.51 V (Table 2), to calculate the formal potential for half-reaction 14, $E^f = 0.88 \text{ V}$



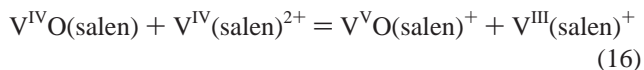
and half reaction 5, $E^f = 0.70 \text{ V}$.

The results (Table 2) show that in the presence of (1 M) acid, V^{IV}O(salen) is a considerably stronger one-electron oxidant than is V^VO(salen)⁺, an observation that accounts for the acid-induced disproportionation of V^{IV}O(salen). In 1 M acid V^{IV}O(salen) is only somewhat more oxidizing than V^{IV}(salen)²⁺ (Table 2); the equilibrium constant calculated for reaction 15 is only 42 M⁻¹.



Thus, it is not surprising that the V^{IV}(salen)²⁺, generated by electro-oxidation of V^{III}(salen)⁺, does not persist in weakly acidified solutions ($[\text{H}^+] \ll 1 \text{ M}$) containing residual H₂O (Scheme 1).

A likely mechanism for the acid-induced disproportionation reaction might begin with the removal of the oxo group from V^{IV}O(salen) by the added acid (reaction 15) followed by a simple, outer-sphere oxidation of a second V^{IV}O(salen) molecule by V^{IV}(salen)²⁺ according to reaction 16 for which an equilibrium constant of 3.8×10^4 can be calculated.



The combination of reactions 15 and 16 accounts for the observed stoichiometry of the disproportionation reaction.

Instability of Mixtures of V^{III}(salen)⁺ and V^VO(salen)⁺. The voltammetric responses obtained with pure solutions of V^{III}(salen)⁺ or V^VO(salen)⁺ are quite stable in the absence of acid. [V^VO(salen)⁺ is equally stable in the presence of acid but V^{III}(salen)⁺ is slowly decomposed by millimolar amounts of acid.] However, when both V^{III}(salen)⁺ and V^VO(salen)⁺ are present, the voltammetric response changes slowly: The plateau currents for the oxidation of V^{III}(salen)⁺ and the reduction of VO(salen)⁺ gradually diminish as a second anodic wave develops that corresponds to the oxidation of V^{IV}O(salen). This behavior reflects more than a slow approach to equilibrium of reaction 2 because the overall magnitude of the plateau currents falls below the values expected for an equilibrated mixture of the three complexes. The ESR spectrum of aged mixtures of V^{III}(salen)⁺ and V^VO(salen)⁺ indicates the presence of both V^{IV}O(salen)

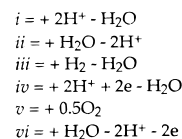
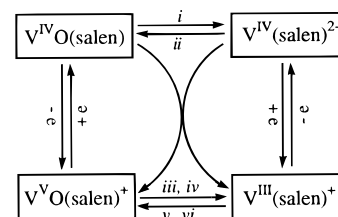
and a second V(IV) complex generated as the mixture decomposes. This behavior can be understood if the $V^{III}(\text{salen})^+$ complex is presumed to decompose in the presence of acid to yield a complex of V(III) that is a stronger reducing agent so that it can reduce $V^VO(\text{salen})^+$ to produce $V^{IV}O(\text{salen})$ and a decomposed complex of V(IV) that is not electroactive in the potential range of interest. This explanation is in accord with the observation that addition of H_2O to mixtures of $V^{III}(\text{salen})^+$ and $V^VO(\text{salen})^+$ accelerates their decomposition as comproportionation (the reverse of reaction 2) generates acid that causes the $V^{III}(\text{salen})^+$ complex to decompose. The smaller plateau currents in curves 3 and 4 of Figure 1 can also be understood on the same basis.

Reactions with O_2 . The reactions in Scheme 2 account for the kinetics observed during the stoichiometric oxidation of $V^{III}(\text{salen})^+$ by O_2 . The proposed formation of a $O_2V(\text{salen})^+$ complex in reaction 9 has precedent in the results of Swinehart, who examined the reaction of $V(\text{salen})^+$ with O_2 in pyridine.¹³ However, in this solvent, the oxidation proceeds only to $V^{IV}O(\text{salen})$.

The reactions in Scheme 2 occur both in the absence and in the presence of acid, but the reduction of O_2 ceases once all of the $V^{III}(\text{salen})^+$ is oxidized to $V^VO(\text{salen})^+$. However, in the presence of excess acid, the combination of Scheme 2 and the electrochemical regeneration of $V^{III}(\text{salen})^+$ (via half-reaction 3 followed by reaction 2) provides a route for the four-electron electroreduction of O_2 as catalyzed by $V^{IV}O(\text{salen})$. In CH_3CN the rate of this catalytic cycle is too slow to be interesting (probably because CH_3CN molecules coordinated to the axial sites in $V^{III}(\text{salen})^+$ retard reaction 9) and the acid-induced decomposition of the complex is an undesirable side reaction. However, in acidified CH_2Cl_2 the catalytic reduction proceeds readily^{5c} and in even less coordinating solvents the catalytic rate becomes impressive.¹⁴

(13) Swinehart, J. H. *Chem. Commun.* **1991**, 1443.

Scheme 3



Conclusions

The interconversions among the several V(salen) complexes that were demonstrated in this study are summarized in Scheme 3.

They are largely supportive of the acid-induced disproportionation of $V^{IV}O(\text{salen})$ as originally proposed by Bonadies et al.¹ The complex that plays the key role in the four-electron reduction of O_2 was shown to be $V^{III}(\text{salen})^+$, but the rate of the reaction in CH_3CN is too slow to be attractive. However, with suitable modifications of the solvent and salen ligand a catalytically interesting system might be developed. Efforts in this direction are underway.

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(14) Liu, Z.; Anson, F. C. Unpublished results, 1999.