

Catalysis of the Electroreduction of O₂ to H₂O by Vanadium–salen Complexes in Acidified Dichloromethane

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Addition of stoichiometric quantities of trifluoromethanesulfonic (triflic) acid to solutions of V^{IV}O(salen) (H₂-salen = *N,N'*-ethylenedis(salicylideneamine)) in dichloromethane produces the μ -oxo dinuclear vanadium(IV) complex [(salen)V^{IV}OV^{IV}(salen)]²⁺ ([V^{IV}OV^{IV}]²⁺). Addition of significant excesses of triflic acid converts the dimer into [V^{IV}(salen)]²⁺. In dichloromethane solutions containing 0.1 M tetrabutylammonium tetrafluoroborate, the [V^{IV}OV^{IV}]²⁺ complex undergoes disproportionation and dissociation reactions to produce a solution containing an equimolar mixture of V^{IV}O(salen), [V^{III}(salen)]⁺, and [V^{IV}OV^V]³⁺. The oxophilic [V^{III}(salen)]⁺ complex reacts with O₂ to accomplish a four-electron reduction of O₂: 2[V^{III}(salen)]⁺ + O₂ → 2[V^VO(salen)]⁺. These reactions can be exploited to carry out catalytic electroreductions of O₂ to H₂O in acidified dichloromethane solutions of V^{IV}O(salen) at unusually positive potentials.

Introduction

In recent reports, the acid–base, coordination, and redox chemistries of complexes of vanadium in oxidation states III–V with the salen ligand (H₂salen = *N,N'*-ethylenedis(salicylideneamine)) in nonaqueous solvents have been described.^{1–13} Among the useful features of the complexes is their ability to serve as catalysts for the oxidative polymerization of diphenyl disulfide using O₂ as oxidant^{14–19} and the electroreduction of O₂ to H₂O in acidified dichloromethane.¹³ Because the elec-

troreduction of O₂ by four electrons usually requires catalysts (e.g., dimeric²⁰ or multinuclear^{21,22} metalloporphyrin complexes) that are difficult to synthesize, the easily prepared vanadium–salen complexes are attractive as alternative catalysts. In this report, previous preliminary studies^{12,13} have been extended and possible mechanisms for both the stoichiometric four-electron electroreduction of O₂ in acid-free solutions and the catalytic four-electron reduction in the presence of excess acid are proposed.

Experimental Section

Materials. Dichloromethane was purified by distillation. Tetrabutylammonium tetrafluoroborate ((TBA)BF₄) was obtained from Wako Chemical Co. and purified by recrystallization from benzene–ethyl acetate. Trifluoroacetic anhydride and trifluoromethanesulfonic acid were obtained from Kanto Chem. Co. and used as received. (*N,N'*-Ethylenebis(salicylideneaminato))oxovanadium(IV), V^{IV}O(salen), (*N,N'*-ethylenedis(salicylideneaminato))oxovanadium(V) tetrafluoroborate, [V^VO(salen)][BF₄], and (μ -oxo)bis[*N,N'*-ethylenedis(salicylideneaminato))vanadium(IV)] tetrafluoroborate, [(salen)V^{IV}OV^{IV}(salen)]-[BF₄]₂, were prepared as previously described.^{11,13}

Apparatus and Procedures. All measurements were performed at room temperature under an atmosphere of dry argon or dioxygen. Electrochemical measurements were carried out in conventional three-compartment glass cells. The glassy carbon rotating disk electrode (0.074 cm²) was polished before each experiment with 0.05 μ m alumina

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paste. The auxiliary electrode, a coiled platinum wire, was separated from the working solution 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 tetrafluoroborate in dichloromethane, which was placed in the main cell compartment. The formal potential of the ferrocene/ferrocenium couple in dichloromethane was 0.34 V vs this reference electrode. All potentials are quoted with respect to this Ag/AgCl reference electrode. Electrochemical instrumentation was from EG&G Princeton Applied Research, Pine Instrument Co., Houston Instruments, and Bioanalytical Systems. ESR spectra were recorded using a JEOL RE-2XG instrument, ⁵¹V NMR spectra were obtained using a JEOL 400-MHz FT-NMR GX5400 spectrometer, and UV-visible spectra were obtained with a Shimadzu UV-2100 spectrophotometer.

Results and Discussion

Electrochemistry of V^{IV}O(salen) and [(salen)V^{IV}OV^{IV}-(salen)][BF₄]₂. Catalytically active forms of vanadium-salen complexes are available from the easily prepared (*N,N'*-ethylenebis(salicylideneaminato))oxovanadium(IV) complex, V^{IV}O(salen). Cyclic voltammograms for solutions of V^{IV}O(salen) in acetonitrile (or dichloromethane) exhibit a reversible response for the [VO(salen)]⁺⁰ couple.¹¹ This response is unaffected by the presence of O₂, which does not react with V^{IV}O(salen) or [V^{VO}(salen)]⁺ at a significant rate in the absence of acid. Solutions of V^{IV}O(salen) in acid-free dichloromethane exhibit no cathodic electrochemistry at potentials positive of -1.6 V.

Effect of Acid on the Electrochemistry of V^{IV}O(salen). Shown in Figure 1A is the steady-state voltammogram obtained at a rotating glassy carbon disk electrode in a solution of V^{IV}O(salen). The anodic oxidation of V^{IV}O(salen) to [V^{VO}(salen)]⁺ occurs at 0.43 V. Addition of stoichiometric quantities of acid, e.g., trifluoromethanesulfonic (triflic) acid, leads to the formation of an oxo-bridged dimer according to reactions 1 and 2¹¹



where [V^{IV}OV^{IV}]²⁺ ≡ [(salen)V^{IV}OV^{IV}(salen)]²⁺. In dichloromethane the conversion of V^{IV}O(salen) to [V^{IV}OV^{IV}]²⁺ is extensive; the dimeric complex has been isolated as the tetrafluoroborate salt.^{11,13} Steady-state voltammograms at rotating disk electrodes in solutions prepared by dissolving [V^{IV}OV^{IV}][BF₄]₂ in CH₂Cl₂ containing (TBA)BF₄ exhibit a single, composite wave consisting of equal anodic and cathodic plateau currents (solid curve in Figure 1B). Electrolysis of solutions of [V^{IV}OV^{IV}][BF₄]₂ at 0.3 or 0.6 V showed that both the oxidation and the reduction processes involve one electron per molecule of [V^{IV}OV^{IV}][BF₄]₂ dissolved in the initial solution. The presence of a single, composite voltammetric wave in Figure 1B instead of separated oxidation and reduction waves at different potentials suggests that the formal potential of the [VOV]^{3+/2+} couple is less positive than that of the [VOV]^{2+/+} couple so that spontaneous disproportionation of [V^{IV}OV^{IV}]²⁺ into [V^{IV}OV^V]³⁺ and [V^{III}OV^{IV}]⁺ can occur. We found this disproportionation to be extensive in CH₂Cl₂ solutions in the presence of supporting electrolyte, so that the currents in Figure 1B reflect the electrode reactions of the products of the disproportionation reaction rather than those of the [V^{IV}OV^{IV}]²⁺ cation itself.

If significant excesses of acid are added to solutions of [V^{IV}OV^{IV}]²⁺, the dimeric cation undergoes further reaction to produce 2 mol of the [V^{IV}(salen)]²⁺ complex. This acid cleavage

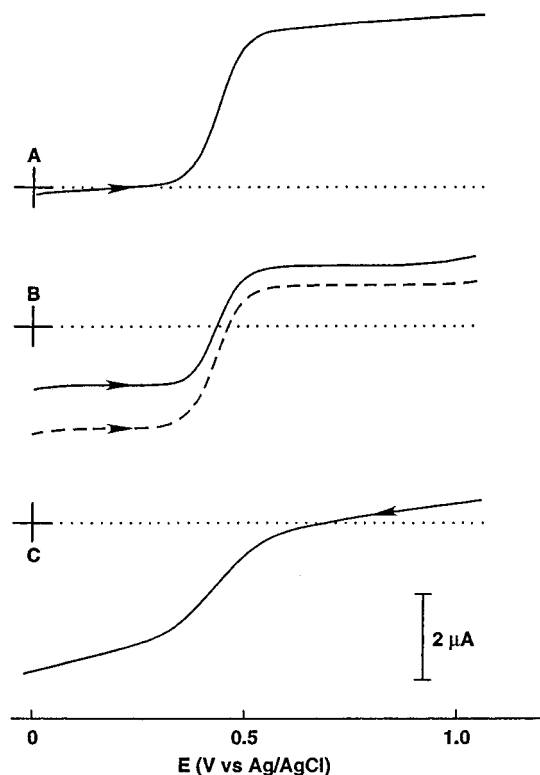
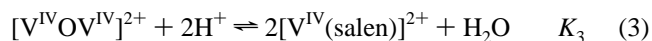


Figure 1. (A) Current-potential curve for a 0.2 mM solution of V^{IV}O(salen) in CH₂Cl₂ saturated with Ar. Supporting electrolyte: 0.1 M (TBA)BF₄. Electrode rotation rate: 100 rpm. Potential scan rate: 5 mV s⁻¹. (B) Key: —, repeat of (A) using 0.1 mM [V^{IV}OV^{IV}][BF₄]₂ in place of 0.2 mM V^{IV}O(salen); - - -, response obtained after a 0.1 mM solution of [V^{IV}OV^{IV}][BF₄]₂ in 0.1 M (TBA)BF₄ in CH₂Cl₂ was saturated with O₂ for 5 min, the O₂ replaced with Ar, and the current-potential curve recorded. (C) Current-potential curve for an Ar-saturated CH₂Cl₂ solution containing 0.2 mM V^{IV}O(salen) and 30 mM CF₃SO₃H as supporting electrolyte. Rotation and scan rates were as in (A).

of [V^{IV}OV^{IV}]²⁺ can be followed with ESR spectroscopy. Addition of stoichiometric quantities (or small stoichiometric excesses) of triflic acid to a solution of V^{IV}O(salen) caused the initial eight-line ESR signal to diminish greatly (Supporting Information) because of magnetic coupling through the oxo bridge in the dimeric [V^{IV}OV^{IV}]²⁺ complex. Addition of excess triflic acid caused a new eight-line spectrum to appear (Supporting Information) that is attributed to [V^{IV}(salen)]²⁺ produced in reaction 3. The *g*₀ value for the [V^{IV}(salen)]²⁺ complex



(1.960) is smaller than that of typical oxo-vanadium(IV) complexes (*g*₀ = 1.97–1.99^{23,24}). This is a feature commonly observed for four-coordinate vanadium(IV) complexes²⁵ and indicates that, under sufficiently acidic conditions, the oxo groups in both V^{IV}O(salen) and [V^{IV}OV^{IV}]²⁺ are removed. A similar small *g*₀ value attributed to the formation of [V^{IV}(salen)]²⁺ was also observed in a previous study of acidified acetonitrile solutions of V^{IV}O(salen).¹¹

To obtain an approximate value for the equilibrium constant for reaction 3, the quantities of V^{IV}O(salen) and [V^{IV}(salen)]²⁺ present in acidified solutions of V^{IV}O(salen) were estimated by integration of the ESR peaks. The results (Supporting Informa-

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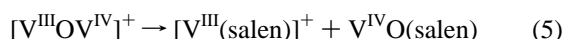
tion) indicated that stoichiometric quantities of protons are adequate for essentially complete conversion of $V^{IV}O(\text{salen})$ into $[V^{IV}OV^{IV}]^{2+}$ at concentrations as low as 0.1 mM while the conversion of $[V^{IV}OV^{IV}]^{2+}$ into $[V^{IV}(\text{salen})]^{2+}$ requires a considerable excess of protons. The ESR data were used to calculate the concentrations of the four reactants involved in reaction 3. A plot of the data (Supporting Information) led to a K_3 value of $\sim 6 \times 10^{-4}$. The relatively small value of this constant reflects the stability of $[V^{IV}OV^{IV}]^{2+}$ toward acid cleavage.

In the presence of sufficient acid to convert both $V^{IV}O(\text{salen})$ and $[V^{IV}OV^{IV}]^{2+}$ to $[V^{IV}(\text{salen})]^{2+}$, e.g., 30 mM triflic acid, the corresponding electrochemical response becomes a single cathodic wave (Figure 1C). The cathodic current results from the reduction of $[V^{IV}(\text{salen})]^{2+}$ to $[V^{III}(\text{salen})]^+$, and the formal potential obtained for the $[V(\text{salen})]^{2+/+}$ couple from the midwave potential in Figure 1C is 0.43 V, essentially the same as the formal potential of the $[VO(\text{salen})]^{+/0}$ couple in CH_2Cl_2 .

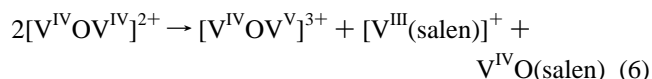
Disproportionation of $[V^{IV}OV^{IV}]^{2+}$. Solutions of $[V^{IV}OV^{IV}]^{2+}$ in CH_2Cl_2 exhibit no ESR signal in the absence of supporting electrolyte but addition of 0.1 M $(\text{TBA})\text{BF}_4$ produces an eight-line spectrum indicating the presence of $V^{IV}O(\text{salen})$. This behavior is consistent with the disproportionation of $[V^{IV}OV^{IV}]^{2+}$ to produce two ESR-silent products (reaction 4),



followed by the spontaneous dissociation of the $[V^{III}OV^{IV}]^+$ complex to produce the ESR-active $V^{IV}O(\text{salen})$ complex and the ESR-silent $[V^{III}(\text{salen})]^+$ complex (reaction 5). Integration



of the ESR signal obtained when 100 $\mu\text{mol/L}$ of $[V^{IV}OV^{IV}][\text{BF}_4]_2$ was dissolved in 0.1 M $(\text{TBA})\text{BF}_4$ in CH_2Cl_2 showed that the resulting solution contained ca. 50 μM $V^{IV}O(\text{salen})$. Thus, the sum of reactions 4 and 5, reaction 6, appears to



proceed essentially to completion in 0.1 M $(\text{TBA})\text{BF}_4$ to produce one reducible and two oxidizable complexes. The effect of supporting electrolyte could be to facilitate the encounter of the two dipositively charged cations involved in the disproportionation of $[V^{IV}OV^{IV}]^{2+}$ or to enhance the dissociation of $[V^{III}OV^{IV}]^+$ by stabilization of the coordinatively unsaturated $[V^{III}(\text{salen})]^+$ complex. The equal anodic and cathodic plateau currents in Figure 1B can then be ascribed to the (simultaneous) one-electron oxidations of $[V^{III}(\text{salen})]^+$ and $V^{IV}O(\text{salen})$ and the two-electron reduction of $[V^{IV}OV^V]^{3+}$, respectively. Because of the spontaneous disproportionation of $[V^{IV}OV^{IV}]^{2+}$ in the presence of supporting electrolyte, the formal potentials of the $[VOV]^{3+/2+}$ and $[VOV]^{2+/+}$ couples cannot be estimated from electrochemical responses such as the one in Figure 1B.

Stoichiometric Reactions of Reduced Vanadium–salen Complexes with O_2 . The reactions between O_2 and the vanadium–salen complexes described in the previous sections are influenced by a variety of factors including the presence or absence of supporting electrolyte, acid, or water and the identity of the nonaqueous solvent employed. Some relevant experimental observations and their interpretations are as follows:

(i) The solubility of $[V^{IV}OV^{IV}][\text{BF}_4]_2$ in CH_2Cl_2 is low in the absence of supporting electrolyte. O_2 is reduced only slowly in such solutions, but in the presence of 0.1 M $(\text{TBA})\text{BF}_4$, a

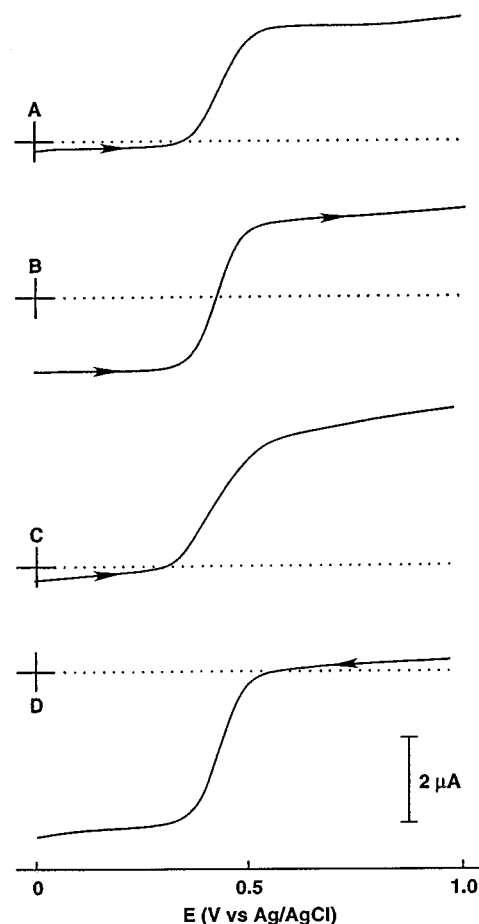


Figure 2. (A) Current–potential curve for the solution resulting from the electrolytic reduction of 0.1 mM $[V^{IV}OV^{IV}][\text{BF}_4]_2$ at 0.3 V in Ar-saturated CH_2Cl_2 containing 0.1 M $(\text{TBA})\text{BF}_4$ and 3 mM $(\text{CF}_3\text{CO})_2\text{O}$. One electron per $[V^{IV}OV^{IV}]^{2+}$ complex was consumed during the electrolysis. (B) Current–potential curve recorded after the solution from (A) was saturated with O_2 for 1 min and the O_2 replaced again with Ar. (C) Current–potential curve obtained for the solution resulting from the electrolytic reduction at 0.3 V of a 0.2 mM solution of $V^{IV}O(\text{salen})$ in Ar-saturated CH_2Cl_2 also containing 1 mM $\text{CF}_3\text{SO}_3\text{H}$, 3 mM $(\text{CF}_3\text{CO})_2\text{O}$, and 0.1 M $(\text{TBA})\text{BF}_4$. One electron per $V^{IV}O(\text{salen})$ complex was consumed during the electrolysis. (D) Current–potential curve recorded after the solution from (C) was saturated with O_2 for 1 min and the O_2 replaced again with Ar. Other conditions were as in Figure 1.

more rapid reaction is observed: Solutions of pure $[V^{IV}OV^{IV}][\text{BF}_4]_2$ in CH_2Cl_2 were stirred under O_2 for several minutes, followed by replacement of the O_2 with Ar and addition of 0.1 M $(\text{TBA})\text{BF}_4$. Current–potential curves recorded for such solutions resembled the solid curve in Figure 1B obtained with a solution of $[V^{IV}OV^{IV}][\text{BF}_4]_2$ that had never been exposed to O_2 . However, if the 0.1 M supporting electrolyte was present during the period that the solution of $[V^{IV}OV^{IV}][\text{BF}_4]_2$ was exposed to O_2 , the current–potential curve recorded after the O_2 was replaced by Ar is shown by the dashed curve in Figure 1B. The anodic to cathodic current ratio was changed to about 1:3, indicating that some of the oxidizable products of reaction 6 had been oxidized by O_2 .

(ii) Electrolytic reduction of a solution of $[V^{IV}OV^{IV}][\text{BF}_4]_2$ under Ar consumed one electron per original $[V^{IV}OV^{IV}]^{2+}$ complex, and the resulting solution exhibited a single, anodic wave at the position corresponding to the essentially equal formal potentials of the $[VO(\text{salen})]^{+/0}$ and $[V(\text{salen})]^{2+/+}$ couples (Figure 2A). The spontaneous disproportionation of $[V^{IV}OV^{IV}]^{2+}$ (reaction 4) requires that the (unmeasurable) formal

potential of the [VOV]^{2+/+} couple be more positive than that of the [VOV]^{3+/2+} couple. Thus, at any potential where [V^{IV}OV^{IV}]²⁺ is being electrolytically reduced (to [V^{III}OV^{IV}]⁺), [V^{IV}OV^V]³⁺ would also be reduced (reaction 7), so that, during the

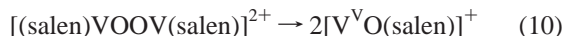
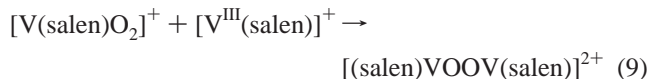


electrolysis, the [V^{IV}OV^V]³⁺ formed in reaction 6 would undergo reduction to [V^{III}OV^{IV}]⁺, which would subsequently be converted to [V^{III}(salen)]⁺ and V^{IV}O(salen) via reaction 5.

It follows from reactions 4–7 that reduced solutions of [V^{IV}OV^{IV}][BF₄]₂ contain an equimolar mixture of V^{IV}O(salen) and [V^{III}(salen)]⁺. Such solutions react only slowly with O₂ unless residual water has been removed from the solvent/supporting electrolyte by addition of an acid anhydride such as (CF₃CO)₂O. (CF₃COOH was observed to be much less potent than CF₃SO₃H in stripping the oxo groups from V^{IV}O(salen) and [V^{IV}OV^{IV}]²⁺.) In dehydrated solutions of [V^{III}(salen)]⁺, a rapid reaction with O₂ ensues and the electrochemical response changes to that shown in Figure 2B, consistent with the presence of an equimolar mixture of V^{IV}O(salen) and [V^{VO}(salen)]⁺. The behavior shown in Figure 2A,B reflects a high reactivity of the four-coordinate, oxophilic [V^{III}(salen)]⁺ complex. In the presence of residual H₂O, the complex can aquate and the coordinated water may ionize to produce a stable hydroxy complex^{26,27} that blocks the coordination site employed by oxidants such as O₂ that prefer inner-sphere transition states.

Additional evidence supporting this interpretation is given in Figure 2C,D. The current–potential curve shown in Figure 2C was recorded with a solution of [V^{III}(salen)]⁺ prepared by electrolytic reduction of [V^{IV}(salen)]²⁺ obtained by reacting V^{IV}O(salen) with excess triflic acid in the presence of trifluoroacetic anhydride. The single, anodic wave corresponds to the oxidation of [V^{III}(salen)]⁺ to [V^{IV}(salen)]²⁺. A rapid reaction occurred when the reduced solution was exposed to O₂, and the new current–potential response obtained after the reaction was complete is shown in Figure 2D. The single, cathodic wave (recorded under Ar) corresponds to the reduction of [V^{VO}(salen)]⁺ to V^{IV}O(salen).

(iii) Electrolytic reduction of a solution of [V^{IV}OV^{IV}][BF₄]₂ under an atmosphere of O₂ instead of Ar consumed two electrons per original [V^{IV}OV^{IV}]²⁺ complex and produced only V^{IV}O(salen) as judged from the eight-line ESR spectrum of the reduced solution and its electrochemical response, which was identical to Figure 1A, with a single anodic wave at the potential expected for the [VO(salen)]⁺⁰ couple. This is the result to be expected if the [V^{III}(salen)]⁺ cation (produced in reaction 6) reacts rapidly with O₂ according to reactions 8–10. The [V^{VO}(salen)]⁺ produced in reaction 10 is then electroreduced to V^{IV}O(salen), and the electrolysis stops with the consumption of two electrons per original [V^{IV}OV^{IV}]²⁺ cation, as observed; for every



[V^{VO}(salen)]⁺ produced in reaction 10 is then electroreduced to V^{IV}O(salen), and the electrolysis stops with the consumption of two electrons per original [V^{IV}OV^{IV}]²⁺ cation, as observed; for every

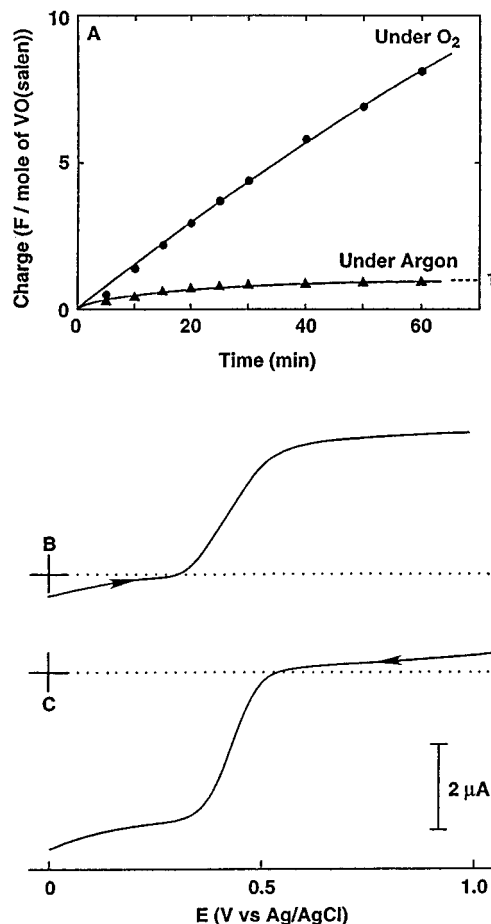


Figure 3. (A) Cathodic charge consumed per mole of vanadium present during the electrolysis of a 0.2 mM solution of V^{IV}O(salen) at a carbon cloth electrode maintained at 0.3 V. Supporting electrolyte: 5 mM CF₃SO₃H + 0.1 M (TBA)BF₄ saturated with argon (lower curve) or O₂ (upper curve). (B) Current–potential curve recorded at a rotating disk electrode with the solution obtained after the electrolysis under Ar in (A) was completed. Electrode rotation rate: 100 rpm. Potential scan rate: 5 mV s⁻¹. (C) Repeat of (B) with the solution obtained after the electrolysis under O₂. The O₂ was replaced with Ar before the current–potential curve was recorded.

four electrons consumed, one molecule of O₂ is reduced to the coordinated oxo groups in the stable V^{IV}O(salen) product.

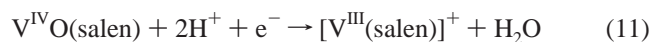
Catalytic Electroreduction of O₂. To render the reduction of O₂ catalytic, it is necessary to regenerate cyclically the [V^{III}(salen)]⁺ complex, which exhibits reactivity toward O₂. This regeneration can be accomplished by the addition of triflic acid to solutions of V^{IV}O(salen), to drive reaction 1 (and 2) to the right, and the addition of supporting electrolyte, to foster the subsequent occurrence of reaction 6. In Figure 3 is shown a comparison of electrolytic reductions at a high-area carbon cloth electrode of acidified solutions of V^{IV}O(salen) under Ar and under O₂. Under Ar, the electrolysis consumes one electron per V^{IV}O(salen) complex and produces a solution of [V^{III}(salen)]⁺, as judged from the lack of an ESR signal from the reduced solution and a single anodic wave at the potential corresponding to the one-electron oxidation of [V^{III}(salen)]⁺ to [V^{IV}(salen)]²⁺ (Figure 3B). Addition of O₂ to the reduced solution caused the anodic wave to become entirely cathodic with a potential corresponding to that of the [VO(salen)]⁺⁰ couple (Figure 3C). The lack of an ESR response from the solution and the coincidence of the UV and ⁵¹V NMR spectra with those of [V^{VO}(salen)][BF₄] (Supporting Information) confirmed that the reaction of [V^{III}(salen)]⁺ with O₂ produced [V^{VO}(salen)]⁺. This

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persistent reactivity of $[\text{V}^{\text{III}}(\text{salen})]^+$ toward O_2 in the presence of acid contrasts with the much weaker reactivity obtained when the $[\text{V}^{\text{III}}(\text{salen})]^+$ was generated in the absence of acid. We attribute this difference to the conversion of the unreactive $\text{V}^{\text{III}}(\text{salen})\text{OH}$ complex (formed by the reaction of $[\text{V}^{\text{III}}(\text{salen})]^+$ with residual H_2O ^{26,27}) into $[\text{V}^{\text{III}}(\text{salen})(\text{OH}_2)]^+$, in which the water molecule occupying the fifth coordination site on the V(III) center can more readily be displaced by O_2 than is possible when hydroxide is the fifth ligand.

Thus, under Ar, the electroreduction of $\text{V}^{\text{IV}}\text{O}(\text{salen})$ in the presence of acid proceeds according to the simple stoichiometry of the half-reaction



However, the mechanism that produces this simple stoichiometry is much more intricate and involves reactions 1, 2, 4, 7, and 5, in that order, because, in the absence of acid, $\text{V}^{\text{IV}}\text{O}(\text{salen})$ itself exhibits no cathodic electrochemistry at potentials more positive than -1.6 V.

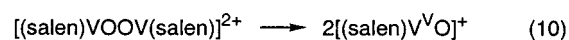
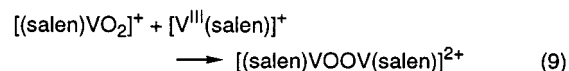
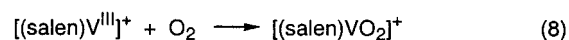
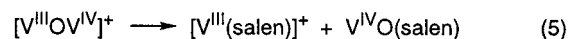
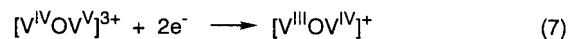
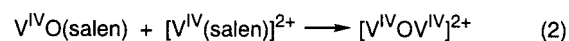
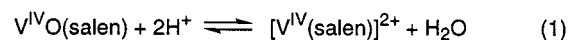
Electrolysis of acidified $\text{V}^{\text{IV}}\text{O}(\text{salen})$ solutions that are saturated with O_2 results in the consumption of many electrons per $\text{V}^{\text{IV}}\text{O}(\text{salen})$ complex (Figure 3A), so that catalytic reduction of O_2 must be involved. A catalytic mechanism consistent with the observed behavior can be constructed from the acid cleavage, disproportionation, and inner-sphere redox reactions already described (Scheme 1). According to the mechanism of Scheme 1, the four-electron reduction of O_2 to two coordinated oxo ligands and, ultimately, to two H_2O molecules is accomplished by the cycling of the V(salen) group between its $[\text{V}^{\text{III}}(\text{salen})]^+$ and $[\text{V}^{\text{V}}\text{O}(\text{salen})]^+$ oxidation states. The breaking of the O–O bond in O_2 is fostered by the oxophilic character of the vanadium(V) state of the catalyst that forms in reaction 10.

Concluding Remarks

This study has identified the reduced, deoxygenated, $[\text{V}^{\text{III}}(\text{salen})]^+$ complex as the essential species in the catalysis of the electroreduction of O_2 by four electrons in CH_2Cl_2 . The binuclear complexes $[\text{V}^{\text{IV}}\text{OV}^{\text{IV}}]^{2+}$ and $[\text{V}^{\text{III}}\text{OV}^{\text{IV}}]^+$, previously proposed as the catalytically active species,¹³ were shown, instead, to be reservoirs from which the active $[\text{V}^{\text{III}}(\text{salen})]^+$ complex is generated by disproportionation of $[\text{V}^{\text{IV}}\text{OV}^{\text{IV}}]^{2+}$ followed by dissociation of $[\text{V}^{\text{III}}\text{OV}^{\text{IV}}]^+$.

The activity of the $[\text{V}^{\text{III}}(\text{salen})]^+$ complex is higher if the CH_2Cl_2 solvent is treated with $(\text{CF}_3\text{CO})_2\text{O}$ because, it is believed,

Scheme 1



coordination of H_2O and, especially, OH^- to the V(III) center interferes with the binding of O_2 to the same coordination site that is required in the inner-sphere, catalytic electron-transfer mechanism. The catalytic mechanism proposed in Scheme 1 for the four-electron reduction of O_2 is a novel one. The possibility that such a mechanism may prove to be generally useful in a variety of autoxidation reactions is the focus of continuing investigations in our laboratories.

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Supporting Information Available: ESR spectra of solutions of $\text{V}^{\text{IV}}\text{O}(\text{salen})$ in the absence and presence of acid, variation of the ratios of initial to final intensities of ESR signals for solutions of $\text{V}^{\text{IV}}\text{O}(\text{salen})$ to which acid was added, and UV and NMR spectra of solutions of $[\text{VO}(\text{salen})][\text{BF}_4]$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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