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Schiff Base Complexes of Vanadium(III, IV, V) as Catalysts for the Electroreduction of O_2 to H_2O in Acetonitrile

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Fifteen Schiff base ligands were synthesized and used to form complexes with vanadium in oxidation states III, IV, and V. Electrochemical and spectral characteristics of the complexes were evaluated and compared. In acidified solutions in acetonitrile the vanadium(IV) complexes undergo reversible disproportionation to form V(III) and V(V) complexes. With several of the ligands the V(III) complexes are much more stable in the presence of acid than is the previously studied complex with salen, an unelaborated Schiff base ligand (H_2 salen = *N*,*N*′-ethylenebis(salicylideneamine)). Equilibrium constants for the disproportionation were evaluated. The vanadium(III) complexes reduce dioxygen to form two oxo ligands. The reaction is stoichiometric in the absence of acid, and second-order rate constants were evaluated. In the presence of acid some of the complexes investigated participate in a catalytic electroreduction of dioxygen.

Introduction

In a recent report[1] the stoichiometric reaction of the vanadium(III) complex of salen, $V^{III}(salen)^+$ (H_2 salen = *N*,*N*′-ethylenebis(salicylideneamine), with O_2 was examined in acetonitrile. The reaction has also been examined in dichloromethane.[2] The possibility that the complex could serve as a catalyst for the four-electron reduction of O_2 in acidified acetonitrile was noted but not pursued because of the instability of $V^{III}(salen)^+$ in the presence of acid and the low rate of its reaction with O_2. The novelty of the chemistry involved in the proposed catalytic mechanism and the likelihood that it could also be applied to the electroreduction of O_2 provided impetus for an expanded study of analogous Schiff base ligands modified to enhance the stability and catalytic activity of their complexes with V(III). In the present study, 15 modified Schiff base ligands and their complexes with vanadium were prepared and examined as potential catalysts for the reduction of O_2. Much greater resistances to acid decomposition were exhibited by some of the complexes, and two reacted with O_2 at rates that exceeded by 7-fold that of $V^{III}(salen)^+$. Spectroscopic and, especially, electrochemical properties of this expanded set of Schiff base complexes of V(III, IV, V) are described in this report. The results may provide a useful foundation on which to base the design of complexes with even greater catalytic reactivities.

Experimental Section

Materials. Distilled acetonitrile containing 0.001% water (EM Science) was stored over 3 Å molecular sieves. Trifluoromethanesulfonic (triflic) acid (Sigma) was used as received. All supporting electrolytes were electrochemical grade (Fluka). They were placed under vacuum at 75 °C overnight before use. The diamines, aromatic aldehydes, and other reagents used in syntheses were obtained from commercial sources and used as received. The Schiff bases and their complexes with vanadium(IV) were prepared according to literature procedures.[3] The Schiff base ligands were prepared by condensing aldehydes with diamines in ethanol. The resulting insoluble ligands could be isolated by filtration but were often used without isolation by adding $VOSO_4$ and refluxing the mixture for ca. 4 h. The resulting oxovanadium(IV) Schiff base complexes were isolated by filtration with typical yields of 70−90%. Complexes that were soluble in dichloromethane (Table S1 of Supporting Information) were recrystallized from dichloromethane−ethanol. The preparative procedure for the complex of Schiff base (SB) no. 1 is representative. To a solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (2.34 g, 10 mmol) in hot ethanol (100 mL), ethylenediamine (0.31 g, 5 mmol) was slowly added. A yellow precipitate was formed immediately. The acid released was neutralized by addition of sodium acetate trihydrate (1.5 g, 11 mmol), and the mixture was stirred for 10 min. (VO) $SO_4 \cdot 4H_2O$ (1.175 g, 5 mmol) dissolved in 20 mL of water was then added dropwise to the suspension, and the mixture was refluxed for ca. 4 h. After the mixture was cooled to room temperature, a green precipitate was collected by filtration (2.5 g, 4.3 mmol, 86%), washed twice with water and ethanol, and dried in vacuo at 70 °C overnight.

Schiff base complexes of V(III) were prepared as previously described[1] by reduction of the corresponding oxovanadium(IV) complexes with H_2 in the presence of a large area Pt gauze and 1 mol of triflic acid per mole of V(IV).

Apparatus and Procedures. Electrochemical measurements were carried out in a conventional one- or two-compartment cell using a BAS model 100B/W electrochemical analyzer. Solutions were kept under an atmosphere of argon that was purified by passage through a gas scrubber (Oxiclear, Aldrich) and two columns filled with molecular sieves. The working electrode in voltammetric experiments was a 10 μm carbon microelectrode, which was polished with 0.3 μm and 0.05 μm alumina paste before use. A porous glassy-carbon working electrode was used for bulk electrolyses. Auxiliary electrodes were platinum wires or foils. The reference electrode was Ag/AgCl in CH_3CN saturated with NaCl. All potentials are quoted with respect to this electrode. The half-wave potentials of the ferrocinium/ferrocene couple measured from microelectrode voltammograms recorded in pure acetonitrile and in a

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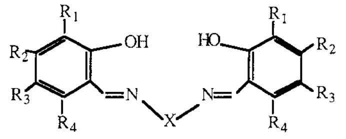
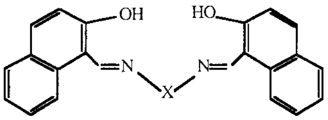
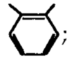
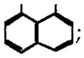
Table 1. Schiff Base Ligands Utilized in This Study



No.	R_1	R_2	R_3	R_4	X
0	H	H	H	H	CH_2CH_2
1	t-Bu	H	t-Bu	H	CH_2CH_2
2	H	H	H	H	1,2-C_6H_4[a]
3	H	H	H	H	$CH_2CH_2CH_2$
4	H	H	NO_2	H	CH_2CH_2
5	H	H	H	H	$CH_2C(CH_3)_2CH_2$
6	H	H	H	H	1,8-$C_{10}H_6$[b]
7	t-Bu	H	t-Bu	H	1,8-$C_{10}H_6$[b]
8	t-Bu	H	t-Bu	H	1,2-C_6H_4[a]
9	H	H	NO_2	H	$CH_2C(CH_3)_2CH_2$
10	H	H	NO_2	H	1,2-C_6H_{10}[c]
11	H	H	MeO	H	CH_2CH_2
12	H	MeO	H	MeO	CH_2CH_2



13	X = CH_2CH_2
14	X = 1,2-C_6H_4[a]
15	X = 1,8-$C_{10}H_6$[b]

a ; b ; c 

0.1 M tetrabutylammonium perchlorate solution in acetonitrile were 0.47 and 0.44 V, respectively, vs this reference electrode.

The rates of the reactions between O_2 and the V(III) complexes of the various Schiff base ligands in acetonitrile solution at 22 ± 2 °C were measured by following the decrease of the anodic plateau current for the complexes measured at the microelectrode. The solutions were kept saturated with O_2 or air during the measurements. Solution IR spectra were obtained using a Perkin-Elmer 1600 FT-IR spectrophotometer and a cell with CaF_2 windows separated by 1 mm. Baselines were obtained using pure acetonitrile. Solid samples were examined as Nujol mulls. EPR spectra were recorded on a Bruker EMX spectrometer operating at X-band. A cylindrical quartz cell with a diameter of 2 mm was used as the sample tube. Elemental analyses were performed by Desert Analytics.

Results

The Complexes. The structures of the Schiff base ligands that were used to form complexes with V(III, IV, V) in this study are given in Table 1. The colors, solubilities, and elemental analyses of the complexes are listed in Table S1 (Supporting Information). The observed and calculated elemental analyses were generally satisfactory, but in a few instances (complexes of ligands 3, 4, 6, 7, and 9) low solubility prevented recrystallization of the complexes, which thwarted efforts to improve their purity. The low solubility has been attributed to the formation of polymeric structures in which $(V{=}O{\rightarrow}V{=}O)_n$ units link the monomeric complexes.[4,5] The factors that favor or disfavor the formation of such polymeric structures remain to be elucidated. Electrochemical experiments were restricted to complexes with satisfactory elemental analyses.

In Table S2 (Supporting Information) are listed the positions of the IR band corresponding to the V=O stretching mode for each complex. Band peaks near 985 cm^{-1} are typical for a large variety of oxovanadium(IV) complexes.[6] The position of this band is similar for both solid and dissolved samples. Band maxima below 900 cm^{-1}, typical for the less soluble complexes (Table S1), have been attributed to interactions among V=O groups in the solid state.[5, 7, 8]

The EPR spectra recorded with solutions of the eight soluble oxovanadium(IV) complexes were similar. They exhibited the eight-line isotropic spectra expected for coupling of the unpaired electron with the ^{51}V nucleus ($I = {}^7/_2$). The g factors and nuclear hyperfine splitting factors are listed in Table S2.

The low solubilities in acetonitrile of almost half of the oxovanadium(IV) complexes of the ligands in Table 1 (nos. 3, 4, 6, 7, 9, 10, 15) prevented investigations of their solution chemistry and electrochemistry. In what follows, we restrict the descriptions to complexes with at least modest solubility in acetonitrile.

Acid-Induced Disproportionation of the Oxovanadium(IV) Complexes. One route to the reduced vanadium(III) Schiff base complexes, $V^{III}(SB)^+$, which react with O_2, is to induce the disproportionation of the corresponding oxovanadium(IV) complexes, $V^{IV}O(SB)$ (SB = Schiff base dianion), by exposing them to acid:[1]

$$2V^{IV}O(SB) + 2H^+ \rightleftharpoons V^{III}(SB)^+ + V^VO(SB)^+ + H_2O \quad (1)$$

To monitor the course of reaction 1, steady-state voltammetry with a carbon microelectrode was employed.[1] In the absence of acid, solutions of all of the soluble $V^{IV}O(SB)$ complexes exhibited a single oxidation step corresponding to the half-reaction:

$$V^{IV}O(SB) - e \rightarrow V^VO(SB)^+ \quad (2)$$

(No reductions of the $V^{IV}O(SB)$ complexes were observed.) For example, curve 1 in Figure 1 is the voltammogram obtained with a solution of $V^{IV}O(SB)$ for SB = ligand 1 in Table 1. (Controlled potential electrolysis at a porous glassy-carbon electrode confirmed that the anodic wave involved a one-electron oxidation to $V^VO(SB)^+$.) Addition of 1.0 mmol per liter of CF_3SO_3H to the solution used to record curve 1 caused the voltammetric response to change to that shown in curve 2. It consists of an anodic wave with a plateau current half as large as that of curve 1 and a more positive half-wave potential. The addition of acid also produced a cathodic wave with a half-wave potential that matched that of the anodic wave of curve 1 and a plateau current that was half as large. These features are exactly those to be expected if the disproportionation in reaction 1 proceeded essentially quantitatively. The cathodic wave in curve 2 corresponds to the reverse of half-reaction 2, and the new anodic wave corresponds to the half-reaction

$$V^{III}(SB)^+ - e \rightarrow V^{IV}(SB)^{2+} \quad (3)$$

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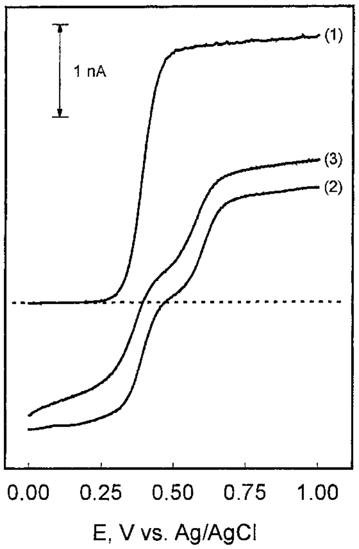

Figure 1. (1) Steady-state current−potential curves recorded with a carbon microelectrode in a 1 mM solution of $V^{IV}O(SB)$ (for SB = ligand 1 in Table 1) in anhydrous CH_3CN containing 0.1 M tetrabutylammonium perchlorate. (2) After 1 mmol per liter of CF_3SO_3H was added to the solution. (3) After the solution used to record curve 2 was made 0.2 M in H_2O. Scan rate = 10 mV s^{-1}. The dotted line marks the position of zero current.

Table 2. Equilibrium Constants for the Acid-Induced Disproportionation of $V^{IV}O(SB)$ According to Reaction 1[a]

SB no.	$[H_2O]$, M	K_1, M^{-1}
1	0.2	$(6 \pm 4) \times 10^7$
2	0.1	$(3.3 \pm 0.3) \times 10^5$
8	0.1	$(1.0 \pm 0.3) \times 10^6$
11	0.2	$(3 \pm 2) \times 10^7$
12	0.2	$(5 \pm 3) \times 10^7$
14	0.02	$(3.0 \pm 0.5) \times 10^5$
14	0.01	$(3.2 \pm 0.6) \times 10^5$

[a] The initial concentration of $V^{IV}O(SB)$ was 1.0 mM except for SB no. 14 where it was (and remained) 0.15 mM. Measurements were conducted at ambient laboratory temperature, 22 ± 2 °C.

Curve 2 was obtained with an initially anhydrous acetonitrile solution. When a large stoichiometric excess of water was added to the solution, the voltammetric response changed to that shown in curve 3. The diminished cathodic plateau current and the presence of two anodic waves are the expected result if the added H_2O caused reaction 1 to come to equilibrium with significant quantities of all three complexes present. This interpretation was supported by the EPR spectra of solutions of $V^{IV}O(SB)$: The initial eight-line spectra disappeared when an equimolar quantity of CF_3SO_3H was added to solutions of the complexes in anhydrous acetonitrile, as expected if reation 1 proceeded extensively from left to right because neither $V^{V}O(SB)^+$ nor $V^{III}(SB)^+$ are EPR-active. Addition of sufficient H_2O to the mixture caused the EPR signal to reappear as the equilibrium of reaction 1 shifted toward the left.

Equilibrium Constants for Reaction 1. The equilibrium constants for the disproportionation of several of the oxovanadium(IV) complexes prepared from ligands in Table 1 were evaluated from electrochemical measurements using a previously described procedure.[1] (The data analysis involves the assumption that the composition of the solution at the electrode surface does not change during the electrochemical measurements.) The values obtained are listed in Table 2. Uncertainties in the values of K_1 for complexes 1, 11, and 12 were larger because calculation of the low equilibrium concentrations of protons becomes less and less certain as the value of K_1 increases. The complex formed by Schiff base 14 has limited solubility in acetonitrile (0.15 mM), but the charged products of its disproportionation are much more soluble. In the evaluation of K_1 for this complex a suspension of the solid rather than a solution was employed. The concentration of $V^{IV}O(SB)$ in the saturated solution was measured, assumed to remain constant throughout the titration and used in the calculation of K_1. Titration data and the equilibrium constant calculated from them for this complex are given in Table S3 (Supporting Information).

Table 3. Formal Potentials of Redox Couples for Schiff Base Complexes of V(III, IV, V)

	E^f vs Ag/AgCl, V[a]			
SB no.	$VO(SB)^{+/0}$ [b]	$V(SB)^{2+/+}$ [b]	half-reaction 4[c]	half-reaction 5[c]
1	0.40	0.60	0.63	0.85
2	0.64	0.95	0.81	0.97
8	0.60	0.72	0.78	0.95
11	0.45	0.62	0.67	0.88
12	0.43	0.70	0.66	0.88
14	0.65	0.90	0.81	0.97

[a] The estimated uncertainties in the potentials were ±10−20 mV. [b] Evaluated from cyclic voltammograms recorded in anhydrous acetonitrile containing 0.1 M tetrabutylammonium perchlorate and 1.0 mM complex (except for SB no. 14; 0.15 mM) and obtained at ambient temperatures, 22 ± 2 °C. [c] Calculated from K_1 (Table 2) and E^f for $VO(SB)^{+/0}$.

Formal Potentials. Formal potentials for the $V^{V}O(SB)^+/V^{IV}O(SB)$ and $V^{IV}(SB)^{2+}/V^{III}(SB)^+$ couples were estimated from (the half-wave potentials of) current−potential responses like those in Figure 1. (Cyclic voltammetric experiments confirmed that the electrode reactions were reversible.) The values obtained are listed in Table 3.

Formal potentials for the half-reactions

$$V^{V}O(SB)^+ + 2H^+ + 2e = V^{III}(SB)^+ + H_2O \qquad (4)$$

and

$$V^{IV}O(SB) + 2H^+ + e = V^{III}(SB)^+ + H_2O \qquad (5)$$

are also given in Table 3. These two formal potentials cannot be measured directly because of the disproportionation of $V^{IV}O(SB)$, but they can be calculated from E^f for the $V^{V}O(SB)^+/V^{IV}O(SB)$ couple and values of K_1 (Table 2).

Reaction of $V^{III}(SB)^+$ with O_2. The soluble complexes of $V^{IV}O(SB)$ were converted to $V^{III}(SB)^+$ by reduction with H_2 (Experimental Section). The reaction of $V^{III}(SB)^+$ with O_2 in anhydrous acetonitrile proceeds according to

$$2V^{III}(SB)^+ + O_2 \rightarrow 2V^{V}O(SB)^+ \qquad (6)$$

The stoichiometry of reaction 6 was established in two ways: (i) An excess of O_2 was added to a solution of $V^{III}(SB)^+$, which produced a quantitative conversion of the complex to $V^{V}O(SB)^+$ as determined by steady-state voltammetry. (ii) Aliquots of an acetonitrile solution that was saturated with O_2 were added to a solution of $V^{III}(SB)^+$ in acetonitrile that had been saturated with argon. The mixture was sealed in a Schlenk tube and allowed to react for 24 h. The resulting solution was analyzed for both $V^{III}(SB)^+$ and $V^{V}O(SB)^+$ voltammetrically. Two moles of $V^{V}O(SB)^+$ were produced and two moles of $V^{III}(SB)^+$ were consumed for each mole of O_2 that had been added.

The kinetics of reaction 6 were monitored electrochemically using a carbon microelectrode held at a potential on the plateau of the anodic wave for the oxidation of $V^{III}(SB)^+$ in solutions containing an excess of O_2. Typical current−time traces are

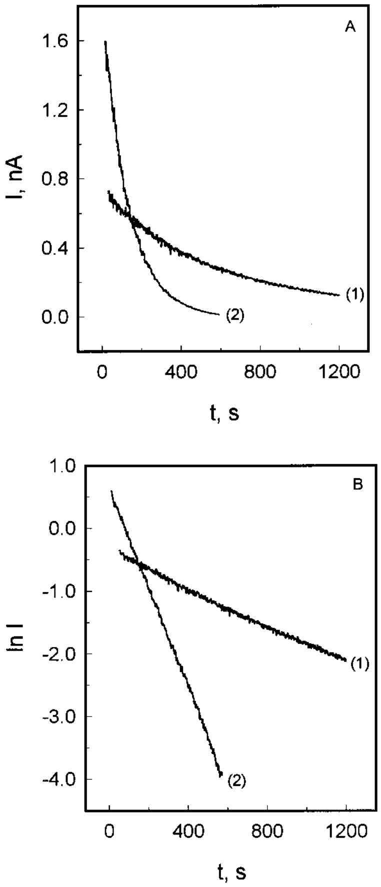

Figure 2. (A) Current−time transients recorded during the reaction of $V^{III}(SB)^+$ (for SB = ligand 1 in Table 1) with O_2 in pure CH_3CN. The anodic current was measured with a carbon microelectrode maintained at 0.8 V. The concentrations of O_2 were 1.7 mM (1) and 8.1 mM (2). The initial concentrations of $V^{III}(SB)^+$ were 0.2 mM (1) and 0.5 mM (2). (B) Pseudo-first-order kinetic plots prepared from the transients in (A). The ratio of the slopes of the plots is 4.8.

shown in Figure 2A, and the corresponding pseudo-first-order kinetic plots are shown in Figure 2B. Data such as those in Figure 2 demonstrated that the rate of reaction 6 is first-order in both $V^{III}(SB)^+$ and O_2. A possible mechanism for the reaction is given in the following reactions.

$$V^{III}(SB)^+ + O_2 \xrightleftharpoons[k_{-7}]{k_7} (SB)V(O_2)^+ \tag{7}$$

$$(SB)V(O_2)^+ + V^{III}(SB)^+ \xrightarrow{k_8} (SB)VO_2V(SB)^{2+} \tag{8}$$

$$(SB)VO_2V(SB)^{2+} \xrightarrow{k_9} 2V^VO(SB)^+ \tag{9}$$

The corresponding rate law when the steady-state approximation is applied to $[(SB)V(O_2)^+]$ and when $k_{-7} \ll k_8[V^{III}(SB)^+]$ is

$$-\frac{d[V^{III}(SB)^+]}{dt} = 2k_7[V^{III}(SB)^+][O_2] \tag{10}$$

Thus, the slopes of the linear plots in Figure 2B correspond to $2k_7[O_2]$. Values of k_7 for the complexes examined are listed in Table 4. The constants span the range from 0.06 to 0.46 M^{-1} s^{-1}, but none was large enough to indicate that a catalytically attractive complex was in hand. The rate of reaction 6 was not affected by the presence of excess acid. Thus, the formation of the proposed $(SB)VO_2^+$ intermediate (reaction 7), supposed to be rate-limiting, is not assisted by the presence of acid.

Table 4. Rate Constants for the Oxidation of $V^{III}(SB)^+$ by O_2[a]

SB no.	k_7, M^{-1} s^{-1}
0	0.060 ± 0.003
1	0.44 ± 0.02
2	0.060 ± 0.003
8	0.46 ± 0.02
11	0.13 ± 0.01
12	0.11 ± 0.01
14	0.090 ± 0.005

[a] Initial concentrations of $V^{III}(SB)^+$ and O_2 were 0.5 and 8.1 mM, respectively. Measurements were made at the ambient laboratory temperature, 22 ± 2 °C.

Discussion

The purpose of this study was to investigate how variations in the structures of Schiff base ligands used to form complexes of V(III, IV and V) affected the reactivities of the complexes, especially in connection with their participation in the reduction of O_2 by the mechanism shown in reactions 7−9.

Preparation of $V^{III}(SB)^+$. To generate $V^{III}(SB)^+$ from the readily available $V^{IV}O(SB)$ or $V^VO(SB)^+$ complexes, a reductive doxygenation is required. Some procedures employed previously for this purpose have used $TiCl_3$ or $SOCl_2$ + Zn dust.[9] These methods inevitably produced chlorovanadium(III) Schiff base complexes. The alternative procedure employed in this and our previous study,[1] which utilizes only 1 equiv of acid, excess H_2, and a large area platinum gauze (on which H_2 is dissociatively adsorbed), was found to be general and efficient. It has the advantage that the $V^{III}(SB)^+$ is produced without extraneous axial ligands that could interfere in reactivity studies.[9−11]

Possible Association of $V^{IV}O(SB)$ and $V^VO(SB)^+$ in Solution. Cyclic voltammograms of $V^{IV}O(SB)$ recorded in acetonitrile are consistent with a simple, uncomplicated reversible conversion to and from $V^VO(SB)^+$. However, voltammograms that are recorded in dichloromethane exhibit evidence of two closely spaced waves.[4] In exploratory experiments not directly related to the present study we have confirmed the results reported in ref 4 but observed that the presence or absence of such double waves depends on not only the solvent but also the concentration of the complex (e.g., the double wave disappears in CH_2Cl_2 at concentrations of $V^{IV}O(salen)$ below ca. 1 mM), the supporting electrolyte employed, and the particular SB ligand employed (e.g., for SB no. 1, which contains four bulky *tert*-butyl groups, no double waves appear in CH_2Cl_2 solutions at concentrations of the complex as great as 10 mM). The behavior observed is consistent with dimerization (or higher oligomerization) of the complexes that exhibit double waves in CH_2Cl_2. Additional experiments are needed to confirm this speculation.

Stoichiometric Reduction of O_2 by $V^{III}(SB)^+$. All of the soluble $V^{III}(SB)^+$ complexes were found to accomplish the stoichiometric reduction of O_2 (to produce two oxo ligands). As can be seen by comparing the rate constants in Table 4 and the formal potentials in Table 3, the strength of $V^{III}(SB)^+$ as a reducing agent (when it is oxidized to $V^VO(SB)^+$) does not correlate with the rate at which it reduces O_2. However, the formal potential of the $V^VO(SB)^+/V^{III}(SB)^+$ couple would not

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be expected to correlate with the rate of reaction 7 because the proposed product of the reaction, $(SB)V(O_2)^+$, does not resemble $(SB)V^VO^+$.

The equilibrium constant for reaction 7 is probably small. The high rate of reaction 8 (and reaction 9) is presumably responsible for the observed quantitative formation of $V^VO(SB)^+$. The chemical step that controls the overall rate, and to which k_7 applies, may involve the dissociation of a solvent molecule from an axial position on the $V^{III}(SB)^+$ complex to generate a coordination site for the incoming O_2 molecule. For example, addition of 2 mM 1-methylimidazole (a good axial ligand) to a solution of $V^{III}(SB)^+$ changed its color from yellow to green and essentially eliminated the reduction of O_2 by the resulting complex of V(III). In addition, with CH_2Cl_2 instead of CH_3CN as solvent, the reaction of $V^{III}(SB)^+$ complexes with O_2 proceeds significantly more rapidly, probably because CH_2Cl_2 competes with O_2 less effectively than does CH_3CN for the axial coordination sites on the catalyst. The larger rate constants exhibited by complexes 1 and 8 (Table 4) may reflect the four tertiary butyl substituents' increasing the lability of ligands coordinated to axial sites on the $V^{III}(SB)^+$ complexes, perhaps because of steric interactions.

Catalytic Reduction of O_2. The mechanism of reactions 7−9 could be made catalytic if the $V^VO(SB)^+$ produced in reaction 9 were reduced (either by a homogeneous reductant or at an electrode) to $V^{IV}O(SB)$ and acid were present in the solution to induce the disproportionation of the $V^{IV}O(SB)$ (reaction 1). Such a scheme was mentioned in our previous study of the $V^{III}(salen)^+$ complex,[1] but the instability of this complex in acetonitrile in the presence of acid prevented the testing of this scheme. Several of the complexes examined in the present study are much more stable in acidic solutions, so the possible catalytic electroreduction of O_2 was explored. The $V^{IV}O(SB)$ complex with SB = ligand 8 (Table 1) was dissolved in acidified acetonitrile saturated with Ar to obtain an equimolar mixture of $V^{III}(SB)^+$ and $V^VO(SB)^+$. A porous glassy-carbon electrode was introduced into the solution to carry out the electroreduction of $V^VO(SB)^+$ to $V^{III}(SB)^+$ (via $V^{IV}O(SB)$ and reaction 1). The cathodic charge consumed in this reduction, shown in curve 1 in the inset of Figure 3, corresponds to one electron per vanadium in the starting $V^{IV}O(SB)$ complex. When a similar electrolysis was carried out with O_2-saturated acetonitrile, the cathodic charge consumed was much greater (curve 2 in the inset in Figure 3). The flow of charge decreased to background levels (plateaus in curve 2) only after all of the acid present was consumed in the reduction of O_2 to H_2O by the combination of reactions 7−9, the inverse of half-reaction 2 and reaction 1 (Scheme 1). The catalytic electroreduction resumed when additional acid was provided whereupon additional cathodic charge was consumed (curve 2 in Figure 3). More than 60 turn-overs of the vanadium Schiff base catalyst occurred during the recording of curve 2 in Figure 3 without significant decomposition of the catalyst. By contrast, when the same experiment was performed using $V^{IV}O(salen)$ (complex 0 in Table 1) as the catalyst, the charge flow ceased even before one electron per vanadium has been consumed and well before all of the acid was consumed (curve 3 in the inset of Figure 3). We attribute this difference in behavior to a more rapid, acid-induced decomposition of $V^{III}(salen)^+$ than of the other tested complexes. The complexes of ligands 2, 8, and 14 (Table 1) all exhibited stability in the presence of acid that was adequate to provide sustained catalytic electroreductions of O_2. However, with none of the complexes was the rate of the overall reduction reaction high enough to be attractive for electrocatalytic applications.

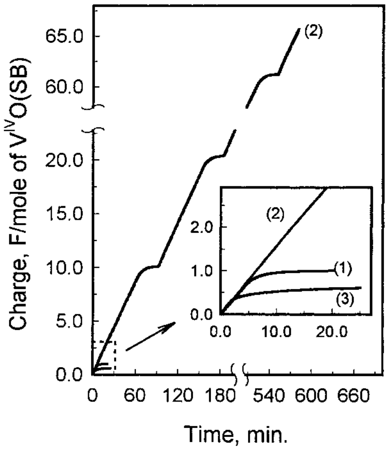
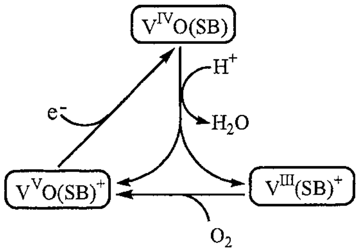


Figure 3. Cathodic charge flow during the electrolytic reductions at 0.55 V of stirred acetonitrile solutions prepared by adding 0.5 mmol per liter of $V^{IV}O(SB)$ (SB = ligand 8 in Table 1) to 5.0 mM CF_3SO_3H. (1) Solution saturated with Ar. (2) Repeat of (1) with an O_2-saturated solution. Additional aliquots of CF_3SO_3H were added to the solution to cause the charge flow to resume after the electrolysis had consumed all of the acid present. (3) Repeat of (2) using $V^{IV}O(salen)$ instead of $V^{IV}O(SB)$. The electrolysis potential was 0.45 V. Supporting electrolyte throughout: 0.1 M tetrabutylammonium perchlorate. Schiff base complexes of oxovanadium(IV), $V^{IV}O(SB)$, disproportionate in acidified acetonitrile to yield $V^VO(SB)^+$ and $V^{III}(SB)^+$. The latter complex reduces O_2 to form (two) $V^VO(SB)^+$ complexes whose electroreduction to $V^{IV}O(SB)$ completes a catalytic cycle in which the four-electron reduction of O_2 proceeds until the supply of either O_2 or H^+ is exhausted.

Scheme 1



Conclusions

The Schiff base ligands in Table 1 form oxovanadium(IV) complexes with similar properties that include reversible oxidation to oxovanadium(V) at potentials between 0.4 and 0.6 V and reversible disproportionation to V(III) and V(V) in the presence of acid in a reaction (reaction 1) that is governed by equilibrium constants of $\sim 10^5 - 10^8$ M^{-1}. In the absence of acid, the deoxygenated vanadium(III) complexes react relatively slowly with O_2 (Table 4) to produce 2 mol of the oxovanadium(V) complexes. In the presence of acid, several of the complexes can act as catalysts for the electroreduction of O_2 to H_2O without significant decomposition of the catalyst. The mechanism of the catalysis is believed to involve an inner-sphere electron-transfer pathway coupled to the acid-induced disproportionation of the oxovanadium(IV) complex formed as an intermediate in the catalytic cycle.

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Supporting Information Available: Two tables containing analytical, spectral (IR and EPR), and solubility data for the 15 complexes examined in this study, and a table of titration data used to evaluate the equilibrium constant of reaction 1 for Schiff base no. 14. This material is available free of charge via the Internet at http://pubs.acs.org.

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