

Rate enhancements in the four-electron reduction of O₂ by mixtures of vanadium(III) Schiff base complexes and decamethylferrocene in acetonitrile

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Abstract

The otherwise slow reaction between O₂ and decamethylferrocene (DMFc) or (SB)V^{III+} (SB = Schiff base ligand) is significantly accelerated if all three reactants are present. In the absence of acid the reduction of O₂ proceeds stoichiometrically to yield the two oxo groups in (SB)V^{IV}O. In the presence of acid the reaction becomes catalytic and the O₂ is reduced to H₂O. In the presence of excess O₂ the catalytic reaction ceases only when the supply of DMFc or acid is depleted. Investigation of the kinetics of the O₂ reduction processes led to a reaction scheme that accounts for much but not all of the kinetic data. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Catalysis; Dioxygen; Reduction; Vanadium–Schiff base; Decamethylferrocene

1. Introduction

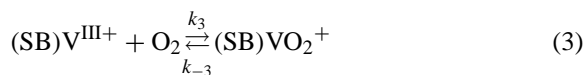
In a recent report [1] we described the four-electron reduction of O₂ in acetonitrile by a set of Schiff base (SB) complexes of vanadium(III), (SB)V^{III+}. The complexes involved various derivatives of the ligand salen (H₂ salen = *N,N'*-ethylenebis(salicylidene-amine)). The stoichiometry of the reduction was shown to be that given in reaction (1) [1]



The rate of the rather slow reduction was shown to follow the rate law given in Eq. (2)

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

with $k = 0.06\text{--}0.5 \text{ M}^{-1} \text{ s}^{-1}$ depending on the particular SB ligand employed [1,2]. The rate-limiting step was proposed to be the coordination of O₂ to the (SB)V^{III+} complex (reaction (3)).



The rate of the reduction of O₂ is substantially enhanced if the auxiliary reducing agent decamethylferrocene (DMFc), is added to the reaction mixture. This was a surprising observation because DMFc does not react with (SB)V^{III+} and its reaction with O₂ is much too slow to account for the reactions observed (although the reaction can be catalyzed by metalloporphyrins [3]). The mechanism of the rate enhancement is of interest because of the possibility

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of the catalysis by vanadium–Schiff base complexes of the four-electron reduction of O_2 . Exploration of the redox chemistry exhibited by the three-component (SB)V^{III+}– O_2 –DMFc system in acetonitrile was the object of this study. Earlier reports [4–6] have described the electrochemical behavior of vanadium–salen complexes.

2. Experimental

2.1. Materials

Distilled acetonitrile containing 0.001% water (EM Science) was stored over 3 Å molecular sieves. Trifluoromethanesulfonic (triflic) acid (Sigma) was used as received. Sublimed decamethylferrocene (Alfa Aesar) was recrystallized from acetonitrile–dichloromethane. All supporting electrolytes were electrochemical grade (Fluka). They were placed under vacuum at 75 °C overnight before use. The diamines, aromatic hydroxaldehydes, and other reagents used in syntheses of the Schiff base ligands were obtained from commercial sources and used as received. The Schiff bases listed in Table 1 and their complexes with oxovanadium(IV) were prepared as described previously [1]. Schiff base complexes of vanadium(III) were prepared

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 mol of V(IV) [1,2].

2.2. Apparatus and procedures

Electrochemical measurements were carried out in conventional one- or two-compartment cells using a BAS model 100B/W electrochemical analyzer. Solutions were kept under an atmosphere of argon that was purified by passing through a gas scrubber (Oxiclear, Aldrich) and two columns filled with molecular sieves. The working electrode used in voltammetric experiments was a 10 μm diameter carbon microelectrode mounted in a glass shroud and polished with 0.3 and 0.05 μm alumina 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 acetonitrile saturated with NaCl. All potentials are quoted with respect to this electrode. Half-wave potentials of the ferrocinium/ferrocene couple measured from microelectrode voltammograms recorded in pure acetonitrile and in 0.1 M tetrabutylammonium perchlorate solutions in acetonitrile were 0.47 and 0.44 V, respectively, versus this reference electrode.

Table 1
Schiff base ligands utilized in this study

No.	R ₁	R ₂	R ₃	R ₄	X
1 ^a	H	H	H	H	CH ₂ CH ₂
2	<i>t</i> -Bu	H	<i>t</i> -Bu	H	CH ₂ CH ₂
3	H	H	H	H	1,2-C ₆ H ₄
4	<i>t</i> -Bu	H	<i>t</i> -Bu	H	1,2-C ₆ H ₄
5	H	H	MeO	H	CH ₂ CH ₂
6	H	MeO	H	MeO	CH ₂ CH ₂
7					
					X=CH ₂ CH ₂

^a This ligand is H₂salen.

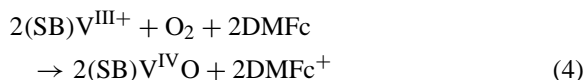
With the exception of kinetic runs, experiments were conducted at ambient laboratory temperature, 22 ± 2 °C.

The kinetics of the reduction of O₂ in mixtures of (SB)V^{III+}, O₂ and DMFc in acetonitrile were measured by monitoring the cathodic plateau current for the reduction of DMFc⁺ (one of the reaction products) at the carbon microelectrode. The solution temperature was maintained at 0 °C by immersing the cell in an ice-water bath. Solutions were usually saturated with either pure O₂ or air throughout the kinetic measurements. Addition of known, limited quantities of O₂ to initially deoxygenated solutions was accomplished by the transfer of measured volumes of O₂-saturated acetonitrile using syringes. The solubility of O₂ in O₂-saturated acetonitrile at 25 °C is 8.1 mM. 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.

3. Results

3.1. Qualitative observations

When (SB)V^{III+} is exposed to excess O₂ in acetonitrile, reaction (1) proceeds slowly but quantitatively. Addition of a stoichiometric quantity of DMFc to the resulting (SB)V^{VO+} complex (in the absence or presence of O₂) rapidly produces (SB)V^{IVO} and DMFc⁺ as expected from the known formal potentials of the (SB)VO^{+/0} and DMFc^{+/0} couples [1], 0.40–0.60 and –0.05 V, respectively. (The reaction between O₂ and DMFc in acetonitrile was negligible under the experimental conditions employed.) These observations might lead one to expect that mixtures containing all three components ((SB)V^{III+}, O₂, DMFc) would react according to reaction (4)



with the overall reaction rate limited by the rate of reaction (1). In fact, mixtures of the three components do react according to the stoichiometry given in reaction (4), but the consumption of O₂ (and (SB)V^{III+}) proceeds much more rapidly than does reaction (1).

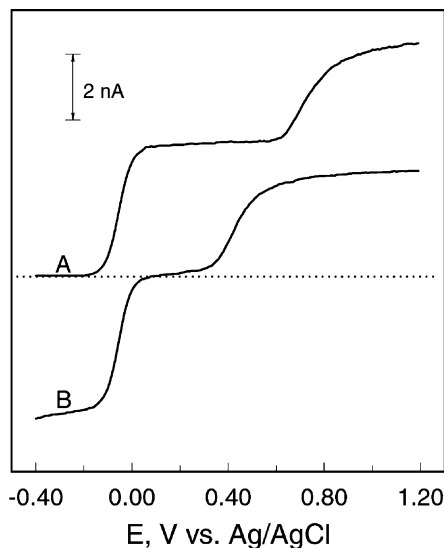


Fig. 1. Steady-state voltammetry at a carbon microelectrode of a mixture of 1 mM (SB)V^{III+} (SB = ligand 2 in Table 1) and 1 mM DMFc in CH₃CN. (A) Solution saturated with argon. (B) After 0.5 mmol per liter of O₂ was injected into the solution. Supporting electrolyte: 10 mM tetrabutylammonium perchlorate (Bu₄NClO₄). Scan rate: 10 mV s⁻¹. For this and the subsequent figures, the position of zero current is shown by the broken line.

3.2. Quantitative observations

To monitor the stoichiometry of the reaction, steady-state voltammetry with a carbon fiber microelectrode was employed as in our previous study [1]. Shown in Fig. 1 are current–potential curves recorded with a solution initially containing equal concentrations of (SB)V^{III+} (SB = ligand 2 in Table 1) and DMFc (curve A). The two anodic plateau currents correspond to the oxidations of DMFc to DMFc⁺ ($E_{1/2} = -0.05$ V) and of (SB)V^{III+} to (SB)V^{IV2+} ($E_{1/2} = 0.75$ V). (The plateau current for the oxidation of DMFc is larger than that for the oxidation of (SB)V^{III+} because of the larger diffusion coefficient of DMFc [2].) Curve B was recorded after 0.5 mol of O₂ per mol of (SB)V^{III+} was added to the solution used to record curve A. The cathodic wave with $E_{1/2} = -0.05$ V results from the reduction of the DMFc⁺ produced in reaction 4. The new anodic wave with $E_{1/2}$ near 0.45 V corresponds to the oxidation of (SB)V^{IVO} (produced by the autoxidation of (SB)V^{III+} to (SB)V^{VO+}). That (SB)V^{IVO} was a

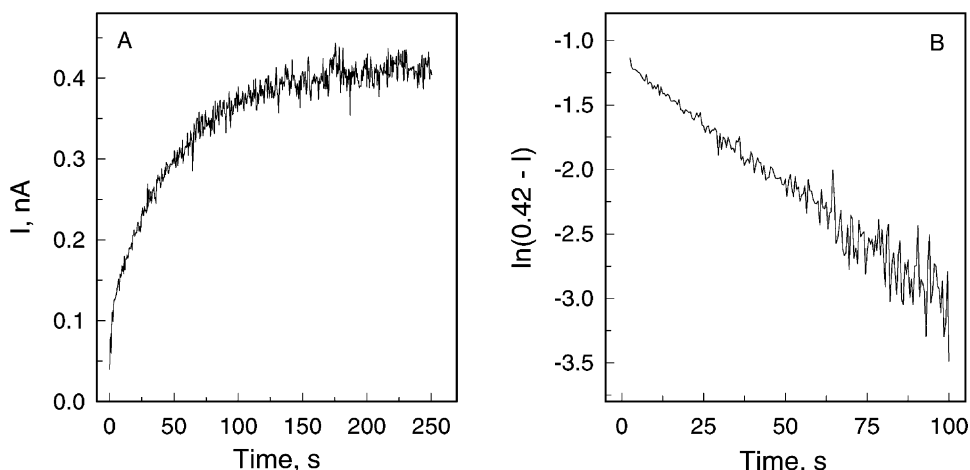


Fig. 2. (A) Current–time curve recorded at 0 °C with a carbon microelectrode held at -0.2 V in O_2 -saturated CH_3CN initially containing 1 mM DMFc and 0.1 mM $(SB)V^{III+}$ (SB = ligand 1 in Table 1) and 10 mM Bu_4NClO_4 . (B) Pseudo first-order kinetic plot of the data from (A). The argument of the logarithm in the ordinate is the difference between the final current, 0.42 nA, and the currents at earlier times, I .

product of the reaction with O_2 was confirmed by the room temperature ESR spectrum of the solution, which exhibited the characteristic eight-line spectrum of vanadium(IV) [1].

3.3. Kinetics of reaction 4

In contrast with reaction (1), the rate of reaction 4 at room temperature was too high to be conveniently measured. However, at 0 °C the reaction rate became low enough to be monitored voltammetrically using the carbon fiber microelectrode. With the electrode potential maintained at -0.2 V, the cathodic current provides a direct measure of the concentration of $DMFc^+$ that is a product of the reaction (Fig. 1, curve B). The course of the reaction was also monitored with the electrode potential set at 0.2 V where the diminishing anodic current reflected the decreasing concentration of DMFc. The rate constant evaluated at either of these potentials was the same. If the electrode potential was set at ca. 0.55 V, the initial anodic current decreased only slightly as the reaction proceeded because the oxidizable DMFc was replaced stoichiometrically by the oxidizable $(SB)V^{IV}O$. The current decrease at this potential reflects only the smaller diffusion coefficient of $(SB)V^{IV}O$ compared with DMFc. However, this result confirmed that the rate of conversion of DMFc to $DMFc^+$ was a reliable

measure of the rate of conversion of $(SB)V^{III+}$ to $(SB)V^{IV}O$ as reaction (4) proceeded.

Shown in Fig. 2A is a typical current–time transient obtained with the microelectrode potential set at -0.2 V during the autoxidation of $(SB)V^{III+}$ (SB = ligand 1 in Table 1) in the presence of excesses of O_2 and DMFc. The cathodic current increased until all of the $(SB)V^{III+}$ was consumed. A typical pseudo first-order plot of such current–time data is shown in Fig. 2B. The slope of the linear plot corresponds to a pseudo first-order rate constant of $0.018\ s^{-1}$. The slopes of such plots did not change when the concentration of DMFc was varied between 0.5 and 2 mM (the solubility of DMFc in CH_3CN at 0 °C). When the concentration of O_2 was decreased five-fold (saturation with air instead of O_2), the pseudo first-order rate constant decreased, but not five-fold (0.018 to $0.012\ s^{-1}$). Thus, with $(salen)V^{III+}$ as the limiting reactant, the reaction rate is independent of the concentration of DMFc and only weakly dependent on the concentration of O_2 .

Similar results were obtained with $(SB)V^{III+}$ complexes with ligands 3, 5–7 in Table 1. With ligands 2 and 4 the pseudo first-order rate was considerably higher; the rate constant was estimated to exceed $0.2\ s^{-1}$. These higher rates have been attributed to enhancement in the rate of reaction (1) when the SB ligands contain bulky substituents [1].

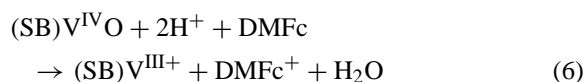
Kinetic experiments conducted with DMFc instead of (SB)V^{III+} as the limiting reactant exhibited more complex behavior: The reaction rate was lower than expected by extrapolation from Fig. 2, the order of mixing of the three reactants affected the reaction rate, and an induction period appeared before the reaction began. Because of these complications, the kinetics of the reaction under these conditions were not pursued.

3.4. Catalysis by (SB)V^{IV}O of the reduction of O₂ by DMFc

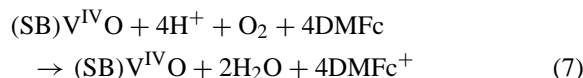
The results described so far were obtained in the absence of acid in the acetonitrile solutions. In the presence of acid (HClO₄ or CF₃SO₃H) an additional reaction pathway apparently becomes available in which the reduction of O₂ by DMFc is catalyzed by (SB)V^{IV}O. It was demonstrated in our previous studies [1,2] that (SB)V^{IV}O disproportionates rapidly in the presence of acid according to reaction (5)



If excess DMFc is also present, it rapidly reduces (SB)V^{VO+} to (SB)V^{IV}O, which can re-enter reaction (5) so that the net reaction becomes



If O₂ is also present in the solution, the (SB)V^{III+} produced in reaction 6 can undergo reaction 4 and a net four-electron reduction of O₂ to H₂O results in which DMFc is the reductant and (SB)V^{IV}O acts as a catalyst (reaction (7)).



Shown in Fig. 3 are microelectrode current–potential responses that demonstrate the chemistry just described. Curve A was recorded in a solution prepared by adding 2 mmol per liter of DMFc, and 1 mmol per liter of (SB)V^{IV}O (SB = salen = ligand 1 in Table 1) to anhydrous acetonitrile. The two anodic waves at –0.05 and 0.6 V correspond to the [DMFc]^{+/0} and [(salen)VO]^{+/0} couples, respectively. Curve B was

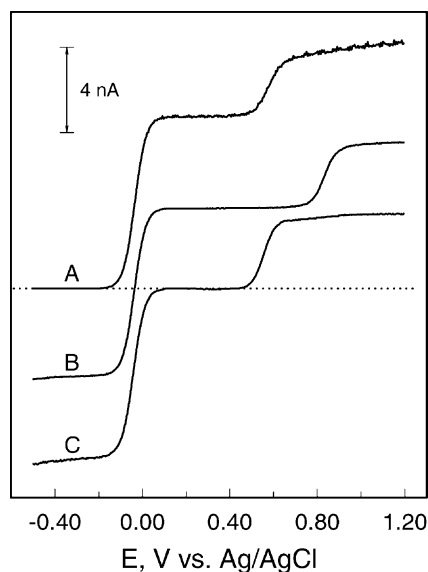


Fig. 3. Steady-state voltammograms recorded with a carbon microelectrode in anhydrous CH₃CN. (A) Solution contained 2 mM DMFc and 1 mM (SB)V^{IV}O (SB = ligand 1 in Table 1). (B) After 2 mmol per liter of CF₃SO₃H were added to the solution used in (A). (C) After 0.5 mol of O₂ per mol of vanadium was added to the solution used in (B). Other conditions as in Fig. 1.

obtained after 2 mmol per liter of CF₃SO₃H were added to the solution used to record curve 1. The three reactants present engaged in reaction (6) to produce a solution that contained 1 mM each of DMFc and DMFc⁺, which are responsible for the composite cathodic–anodic wave at –0.05 V, as well as 1 mM [(salen)V^{III+}]⁺, which gives rise to the anodic wave with E_{1/2} = 0.8 V. Curve C resulted after 0.5 mol of O₂ per mol of vanadium was added to the solution used to record curve B: all of the DMFc was oxidized to DMFc⁺ and all of the (salen)V^{III+} was oxidized to (salen)V^{IV}O (which is electrooxidized to (salen)V^{VO+} at 0.6 V). If all three reactants were added to the acetonitrile at the same time, the response shown in curve C was obtained immediately after mixing because reaction 6 proceeded rapidly until all of the DMFc was consumed.

The catalytic role of (SB)V^{IV}O in the autoxidation of DMFc is confirmed by the results shown in Fig. 4. As aliquots of a solution containing equimolar quantities of DMFc and CF₃SO₃H were added to a dioxygen-saturated solution of (SB)V^{IV}O

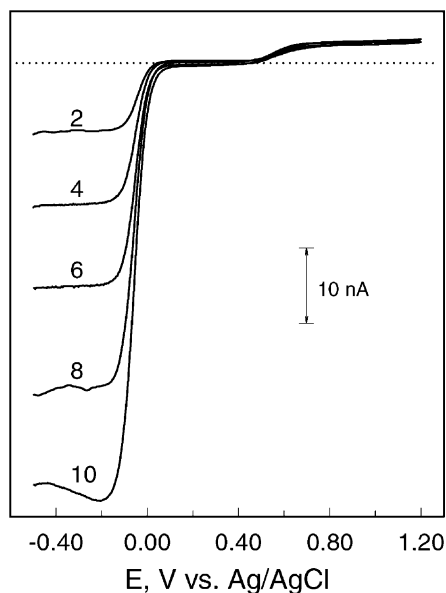


Fig. 4. Steady-state voltammograms recorded with a carbon microelectrode in anhydrous CH_3CN saturated with O_2 and initially containing 1 mM $(\text{SB})\text{V}^{\text{IV}}\text{O}$ (SB = ligand 4 in Table 1). The numbers by each cathodic plateau give the quantities of DMFc and $\text{CF}_3\text{SO}_3\text{H}$ (mmol per liter) that had been added in equimolar amounts to the solution before each curve was recorded.

(SB = ligand 4 in Table 1), the cathodic plateau current arising from reduction of DMFc^+ increased proportionately while the smaller anodic plateau current, corresponding to the oxidation of $(\text{SB})\text{V}^{\text{IV}}\text{O}$, was unaffected by the additions of DMFc and $\text{CF}_3\text{SO}_3\text{H}$. This is the expected behavior if $(\text{SB})\text{V}^{\text{IV}}\text{O}$ participates in reaction (7) only as a catalyst. The persistence of the $(\text{SB})\text{V}^{\text{IV}}\text{O}$ in all of the solutions in Fig. 4 showed that the $\text{CF}_3\text{SO}_3\text{H}$ in each aliquot of the DMFc– $\text{CF}_3\text{SO}_3\text{H}$ mixture was fully consumed in reaction (6). If it were not, the anodic plateau current would have diminished as the acid-promoted disproportionation of $(\text{SB})\text{V}^{\text{IV}}\text{O}$ (reaction (5)) occurred [1].

The amount of H_2O produced in reaction (7) was estimated by means of proton NMR when CD_3CN (dried with 3 \AA molecular sieves) was used as the solvent. Residual CHCD_2CN in the solvent provided a convenient internal standard ($\delta = 1.96 \text{ ppm}$, quintet). The peak for H_2O ($\delta = 2.15 \text{ ppm}$) increased significantly when 20 mmol per liter of both DMFc and $\text{CF}_3\text{SO}_3\text{H}$ were added to a 2 mM solution of $(\text{SB})\text{V}^{\text{IV}}\text{O}$ (SB = ligand 4 in Table 1) saturated with dry O_2 . The area

of the H_2O peak corresponded to 0.55 mol of H_2O per mole of DMFc added, in good agreement with the stoichiometry shown in reaction (7).

The rate of oxidation of DMFc in acidified dioxygen-saturated acetonitrile was also monitored in the absence of $(\text{SB})\text{V}^{\text{IV}}\text{O}$. The reaction was much too slow to have contributed significantly to the production of DMFc^+ during the experiments of Fig. 4.

3.5. Kinetics of the catalytic reaction

The kinetics of the reduction of O_2 by DMFc as catalyzed by $(\text{SB})\text{V}^{\text{IV}}\text{O}$ in the presence of acid were monitored voltammetrically at 0°C using the carbon microelectrode. The electrode was maintained at -0.2 V where the only electrode reaction that occurred was the reduction of DMFc^+ to DMFc (Fig. 3). Shown in Fig. 5 are current–time transients that resulted when small quantities of $(\text{SB})\text{V}^{\text{IV}}\text{O}$ (SB = ligand 7 in Table 1) were added to an acetonitrile

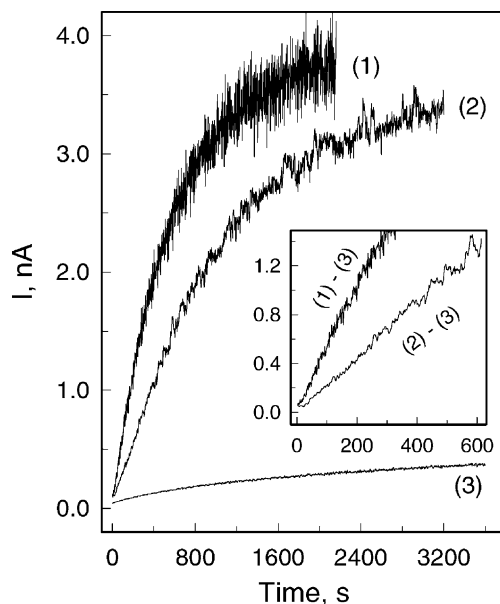


Fig. 5. Current–time curves recorded at 0°C with a carbon microelectrode held at -0.2 V in O_2 -saturated CH_3CN containing 1 mM DMFc, 2 mM $\text{CF}_3\text{SO}_3\text{H}$ and 10 mM Bu_4NClO_4 . The reaction was initiated by the addition of (1) 100, (2) 50, (3) $0 \mu\text{mol}$ per liter of $(\text{SB})\text{V}^{\text{IV}}\text{O}$ (SB = ligand 7 in Table 1) to the solution. Other conditions as in Fig. 2. Inset: plots of the initial portions of curves 1 and 2 after point-by-point subtraction of curve 3 in each case.

solution saturated with O_2 and containing 1 mM DMFc and 2 mM CF_3SO_3H (curves 1 and 2). The much slower rate of the uncatalyzed reduction of O_2 is evident in curve 3. Subtraction (point-by-point) of curve 3 from curve 1 or curve 2 produced the transients shown in the inset in Fig. 5. Only the initial portions of the current–time data were utilized to avoid both the kinetic complexities that are encountered with low concentrations of DMFc (vide supra) and the slow, acid-promoted decomposition of $(SB)V^{IV}O$ and $(SB)V^{III+}$ complexes.

The linearity of the two plots in the inset in Fig. 5 is expected if reaction (7) proceeds while the concentrations of all of the reactants are kept essentially constant. The slopes of the two plots differ by a factor of 2, which matches the ratio of the $(SB)V^{IV}O$ catalyst concentrations in the two experiments. Thus, the catalytic rate law is apparently first-order in the concentration of catalyst, as would be expected if the presence of acid serves only to replenish the supply of $(SB)V^{III+}$ (via rapid reactions (5) and (6)) as it is consumed by reaction with O_2 . Assuming that the reaction rate is independent of the concentration of DMFc, just as it is in the absence of acid (vide supra), the pseudo first-order rate constants calculated from the slopes of curves 1 and 2 in the inset in Fig. 5 are 0.016 and 0.014 s^{-1} , respectively. These values are in reasonable agreement with the rate constant evaluated for the same reactant concentrations but in the absence of acid, 0.018 s^{-1} , which supports the assumption that the addition of acid affects the kinetics only by means of reactions (5) and (6), both of which are much faster than reaction (7).

4. Discussion

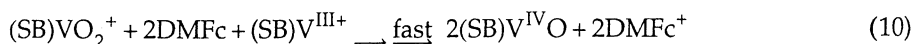
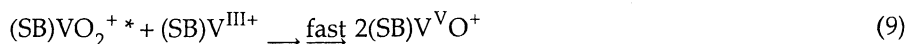
In our previous studies it was shown that O_2 is reduced to two oxo groups by $(SB)V^{III+}$ complexes [1,2]. At room temperature, pseudo first-order rate constants governing the consumption of $(SB)V^{III+}$ in dioxygen-saturated CH_3CN ranged from 5×10^{-4} to $4 \times 10^{-3} s^{-1}$ as the SB ligand was varied. The present study has demonstrated that the presence of 0.5–2 mM DMFc greatly accelerates the reaction rate although the rate enhancement does not depend on the concentration of DMFc in this range. Even at 0 °C much larger rate constants for the consumption of $(SB)V^{III+}$

are obtained in the presence of DMFc than in its absence (0.02–0.2 s^{-1} at 0 °C).

The more rapid consumption of $(SB)V^{III+}$ by O_2 in the presence of DMFc helps to ameliorate the acid-induced decomposition of $(SB)V^{III+}$ complexes that was encountered in our previous studies [1]. In the absence of DMFc, sustained electroreduction of O_2 as catalyzed by $(SB)V^{IV}O$ in the presence of acid was observed only for ligands 3, 4 and 7 in Table 1 because the $(SB)V^{III+}$ complexes of the other ligands were too rapidly destroyed by acid. In contrast, in the presence of DMFc, $(SB)V^{IV}O$ complexes of all of the ligands in Table 1 exhibited sustainable catalytic activity for the electroreduction of O_2 in acidified CH_3CN . With a catalyst concentration of $5 \times 10^{-5} M$ in dioxygen-saturated CH_3CN , turn-over numbers in excess of 60 were obtained with ligands 1, 2, 5 and 6 and over 180 turn-overs were obtained with ligands 3, 4 and 7.

4.1. Mechanism of reaction 4

The results shown in Figs. 1 and 3 clearly established the stoichiometry of reaction (4). In binary mixtures, $(SB)V^{III+}$ reacts slowly with O_2 to produce $(SB)V^{VO+}$ but in the presence of excess DMFc, the reaction is much more rapid and the oxidation product is $(SB)V^{IV}O$ (and $DMFc^+$). The complex behavior obtained in kinetic experiments involving all three reactants thwarted attempts to establish a generally applicable rate law. However, the results obtained were sufficiently reproducible and clear-cut to support some speculations about the reaction chemistry believed to be involved. The three reactants involved in reaction (4) consist of two reductants and one oxidant. Pairwise combination of the oxidant (O_2) with either reductant results only in very slow reactions; all three reactants are required to produce enhanced reaction rates. This behavior indicates that an intermediate formed by reaction between two of the reactants reacts rapidly with the third reactant to produce the rate enhancement. It is unlikely that the reactive intermediate results from the combination of DMFc with either O_2 or $(SB)V^{III+}$ because the electrochemical responses of both O_2 and $(SB)V^{III+}$ are unaffected by the presence of DMFc. The remaining possibility is that the $(SB)VO_2^+$ complex, proposed to be formed in reaction (3), is the reactive intermediate that is reduced more rapidly by



Scheme 1.

DMFc than by $(\text{SB})\text{V}^{\text{III}+}$. This possibility can account for the rate enhancement produced by the presence of DMFc. However, it is not compatible with the mechanistic interpretation offered previously [1,2] in which the forward direction of reaction (3) was assigned as the rate-limiting step, because DMFc could not reduce $(\text{SB})\text{VO}_2^+$ any faster than it was formed. Thus, the present results indicate that a modification in the previous interpretation is called for. A modified mechanism that is compatible with the present results is given in Scheme 1.

The sum of reactions 3, 8 and 9 in Scheme 1 gives reaction (1), which describes the autoxidation of $(\text{SB})\text{V}^{\text{III}+}$ in the absence of DMFc. The key point in Scheme 1 is the introduction of reaction 8 in which the O_2 -vanadium adduct formed in reaction 3 is proposed to undergo an intramolecular transformation (e.g. electron-transfer or a change in hapticity) to produce the oxidant that reacts rapidly with $(\text{SB})\text{V}^{\text{III}+}$ to produce two molecules of $(\text{SB})\text{V}^{\text{VO}+}$ via reaction (9). When reaction (8) is slower than reaction (3), the latter reaction can reach equilibrium and the rate of reaction (1) is expected to exhibit first-order dependences on both O_2 and $(\text{SB})\text{V}^{\text{III}+}$, as observed [2]. Under these circumstances the second-order rate constant evaluated previously in the absence of DMFc and assigned as k_3 [2] would instead be the product k_8K_3 , where K_3 is the equilibrium constant of reaction (3).

In the presence of DMFc the autoxidation of $(\text{SB})\text{V}^{\text{III}+}$ according to reaction (4) can be achieved by combining reactions (3) and (10) of Scheme 1. The acceleration of the overall reaction rate in the presence of DMFc can then be understood as the result of reaction (10) in which $(\text{SB})\text{VO}_2^+$ is reduced rapidly by DMFc (in the presence of $(\text{SB})\text{V}^{\text{III}+}$) without having

to undergo the slower intramolecular transformation depicted in reaction (8). Scheme 1 is compatible with the rate law of Eq. (2) in the absence of DMFc as well as the observed independence of the rate of the DMFc-enhanced reaction on the concentration of DMFc (present in stoichiometric excess). However, some aspects of the observed behavior remain to be explained.

The magnitude of the equilibrium constant, K_3 , is unknown, but it cannot be very large because no evidence of saturation kinetics was obtained (in the absence of DMFc) when $[\text{O}_2]$ was increased from 1.6 to 8 mM at room temperature. The experiments in the presence of DMFc were carried out at 0°C (to diminish the reaction rates to easily measurable values) and it is uncertain that reaction (3) remains at equilibrium under these conditions because of the high rate of reaction (10). The precise nature of reaction (8) and the reason (other than an increase in driving force) that DMFc is able to reduce $(\text{SB})\text{VO}_2^+$ readily while $(\text{SB})\text{V}^{\text{III}+}$ is not, also remain to be explained.

An additional complication in the reaction kinetics was encountered when they were measured in the presence of stoichiometric excesses of both $(\text{SB})\text{V}^{\text{III}+}$ and DMFc with O_2 as the limiting reactant. Under these conditions the overall reaction rate became so much lower that it could be monitored at room temperature. The source of this anomaly was not identified, but the behavior could possibly reflect the formation of a dioxo-bridged dimeric vanadium complex with considerably diminished reactivity toward DMFc. The existence of such a dimer was speculatively suggested in our earlier study [1], and it would be expected to become more important as the molar ratio of vanadium to O_2 increased.

5. Conclusions

Although [Scheme 1](#) does not account for all of the observed kinetic behavior, it provides a reasonable basis for understanding the pattern of reactivity of the (SB)V^{III+}/O₂/DMFc system. In particular, the chemistry by which (SB)V^{III+} reduces O₂ stoichiometrically to oxo ligands (in (SB)V^{IV}O or (SB)V^VO⁺) is accounted for as is the ability of DMFc to enhance the rate of this reaction. The combination of [Scheme 1](#) with the previously demonstrated acid-induced disproportionation of (SB)V^{IV}O (reaction (5)) [1], followed by the rapid reduction of (SB)V^VO⁺ by DMFc (reaction (6)) provides a reasonable explanation for the observed ability of (SB)V^{IV}O to catalyze the reduction of O₂ to H₂O by DMFc in acidified solutions.

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