Inorg. Chem. **1994,** *33,* 1638–1643

Irreversible Electrocatalyic Reduction of V(V) to V(IV) Using Phosphomolybdic Acid

Michael S. Freund and Nathan S. Lewis[*]

Division of Chemistry and Chemical Engineering,[†]
California Institute of Technology, Pasadena, California 91125

Received January 28, 1993[●]

Although VO_2^+(aq) reduction is kinetically slow at glassy carbon and Pt electrodes, phosphomolybdic acid is shown to catalyze the electrochemical reduction of VO_2^+(aq) to VO^{2+}(aq) in 1.0 M H_2SO_4(aq). A second-order rate constant of 33 M^{-1} s^{-1} was observed for this process. ^{31}P NMR spectra demonstrated that $PMo_{11}VO_{40}^{4-}$ and $PMo_{10}V_2O_{40}^{5-}$ were the dominant P-containing species under electrocatalytic conditions. The incorporation of V^V into the polyoxoanion led to a shift in potential from $E°(VO_2^+(aq)/VO^{2+}(aq)) = +0.80$ V *vs* Ag/AgCl for free V^V/V^{IV} to $E°' = +0.55$ V *vs* Ag/AgCl for V^V/V^{IV} bound in the heteropolyoxometalate ($PMo_{11}VO_{40}^{4-}$). This shift in formal potential corresponded to an equilibrium constant of 1.7×10^4 M^{-1} for preferential binding of V^V over V^{IV} by the heteropolyoxoanion. This negative shift in redox potential, combined with the slow electrochemical kinetics of free VO_2^+(aq) reduction and with the facile reaction of bound V^{IV} with free V^V in 1.0 M H_2SO_4(aq), resulted in the irreversible electrocatalytic reduction of VO_2^+(aq) to VO^{2+}(aq).

Introduction

Heteropolyoxometalates[1] are of considerable interest as redox catalysts.[2] The reversibility of redox reactions involving heteropolyoxometalates, combined with the facile reoxidation of many reduced heteropolyoxometalates by O_2, has resulted in their use as catalysts in a variety of oxidation reactions.[2] For example, there has been considerable interest in the use of heteropolyoxometalates in Wacker-type oxidation reactions.[3] Heteropolyoxometalates have also been employed for the modification of electrode surfaces and for catalyzing electrochemical reactions such as proton reduction and nitrite and nitric oxide reduction to ammonia.[4]

One attractive feature of heteropolyoxometalates is that the properties of these clusters can be altered systematically. For example, heteropolyoxoanions with Keggin structures have differing degrees of stability in aqueous solution, depending on whether the polyoxoanions contain Mo^{VI} or W^{VI}.[1,2] In addition, the redox potentials of the heteropolyoxometalate can be manipulated by replacing Mo^{VI} or W^{VI} with pentavalent vanadium.[1,2] These properties are important in the use of heteropolyoxometalates as redox catalysts[1–4] and may have implications toward understanding vanadium redox behavior in biological systems that involve the formation of octahedral V^V.[5] For example, the proposed structure for the active site in vanadium bromoperoxidase consists of V^V coordinated by oxygen donor atoms, resulting in a coordination sphere with a distorted octahedral symmetry[5c] as is observed in heteropolyoxometalates.[6]

In this work, electrochemical methods have been used to show that phosphomolybdic acid ($H_3PMo_{12}O_{40}$) rapidly incorporates V^V and catalyzes VO_2^+(aq) reduction. $PMo_{12}O_{40}^{3-}$ has been reported previously to be in equilibrium with Mo^{VI} and phosphate in aqueous solution, thus providing a labile site for potential binding of the V^V substrate.[1] Additionally, V^V can replace Mo^{VI} to form a mixed heteropolyoxometalate $PMo_{12-n}V_nO_{40}^{(3+n)-}$ while maintaining the Keggin structure.[1,2] Furthermore, reduction of $PMo_{12-n}V_nO_{40}^{(3+n)-}$ results in the localization of electrons on vanadium and does not affect the oxidation state of Mo in the Keggin structure.[6] Under these conditions, the oxidized heteropolyoxometalate can be considered as an acceptor ligand binding pentavalent V^V,[1c,6b] so reduction of this complex could provide a facile kinetic pathway for catalyzing the reduction of VO_2^+(aq) to VO^{2+}(aq).

In an aqueous H_2SO_4 solution with a 1:1 ratio of $[VO_2^+(aq)]$:$[PMo_{12}O_{40}^{3-}]$, we observe that the molybdovanadophosphoric acid is stable and demonstrates well-behaved redox chemistry without significant loss of V from the Keggin structure upon reduction. ^{31}P NMR spectra have verified that the dominant forms of the polyoxoanion are $PMo_{11}VO_{40}^{4-}$ and $PMo_{10}V_2O_{40}^{5-}$. When VO_2^+(aq) is in excess (i.e. greater than a 1:1 ratio of $[VO_2^+]$:$[PMo_{12}O_{40}^{3-}]$), the reduced molybdovanadophosphoric acid is reoxidized by free VO_2^+(aq), resulting in the catalytic reduction of VO_2^+(aq) to VO^{2+}(aq). In contrast, bulk electrolysis of VO_2^+(aq) in the presence of $PMo_{12}O_{40}^{3-}$ ($[VO_2^+]$:$[PMo_{12}O_{40}^{3-}]$ = 10:1) shows that V in the oxidized heteropolyanion does not effect the oxidation of VO^{2+}(aq). The irreversibility of the catalytic reduction of VO_2^+(aq) is consistent with the observed preferential binding of V^V over V^{IV} into the Keggin structure. In this sense, molybdovanadophosphoric acid acts as a molecular diode, allowing the reduction of VO_2^+(aq) while prohibiting its

---

[*] Author to whom correspondence should be addressed.

[†] Contribution No. 8794.

[●] Abstract published in *Advance ACS Abstracts,* February 15, 1994.

(1) (a) Weakley, T. J. R. *Struct. Bonding* **1974**, *18*, 131–176. (b) Pope, M.T. *Heteropoly and Isopoly Oxometalates*; Springer: New York, 1983. (c) Pope, M. T.; Muller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34–48.

(2) (a) Kozhevnikov, I. V.; Matveev, K. I. *Appl. Catal.* **1983**, *5*, 135–150. (b) Misono, M. *Catal. Rev.—Sci. Eng.* **1987**, *29*, 269–321. (c) Griffith, W. P. *Transition Met. Chem.* (*London*) **1991**, *16*, 548–552.

(3) (a) Matveev, K. I. *Kinet. Catal.* **1977**, *18*, 716–728. (b) Davison, S. F.; Mann, B.E.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1223–1228. (c) Golodov, V. A.; Jumakaeva, B. S. *J. Mol. Catal.* **1986**, *35*, 309–315. (d) Grate, J. H.; Hamm, D. R.; Mahajan, S. Unpublished results. (e) Neumann, R.; Levin, M. *J. Am. Chem. Soc.* **1992**, *114*, 7278–7276. (f) Freund, M. S.; Labinger, J. A.; Lewis, N. S.; Bercaw, J. E. *J. Mol. Catal.*, in press.

(4) (a) Dong, S.; Jin, Z. *J. Chem. Soc., Chem. Commun.* **1987**, 1871–1872. (b) Keita, B.; Nadjo, L.; Savéant, J.-M. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *243*, 105–116. (c) Kulesza, P. J.; Faulkner, L. R. *J. Electroanal. Chem. Interfacial Electrochem.* **1989**, *259*, 81–98. (d) Keita, B.; Essaadi, K.; Nadjo, L. *J. Electroanal. Chem. Interfacial Electrochem.* **1989**, *259*, 127–146. (e) Toth, J. E.; Anson, F. C. *J. Am. Chem. Soc.* **1989**, *111*, 2444–2451. (f) Dong, S.; Song. F.; Wang, B.; Liu, B. *Electroanalysis* **1992**, *4*, 643–646.

(5) (a) Nawi, M. A.; Riechel, T. L. *Inorg. Chim. Acta* **1987**, *136*, 33–39. (b) Wever, R.; Kustin, K. *Adv. Inorg. Chem.* **1990**, *35*, 81–116. (c) Holmes, S.; Carrano, C. J. *Inorg. Chem.* **1991**, *30*, 1231–1235. (d) Crans, D. C.; Ehde, P. M.; Shin, P. K.; Pettersson, L. *J. Am. Chem. Soc.* **1991**, *113*, 3728–3736. (e) Michibata, H.; Morita, A.; Kanamori, K. *Biol. Bull.* **1991**, *181*, 189–194. (f) Cornman, C. R.; Kampf, J.; Pecoraro, V. L. *Inorg. Chem.* **1992**, *31*, 1981–1983.

(6) (a) Pope, M. T. *Inorg. Chem.* **1972**, *11*, 1973–1974. (b) Altenau, J. J.; Pope, M. T.; Prados, R. A.; So, H. *Inorg. Chem.* **1975**, *14*, 417–421.

0020-1669/94/1333-1638$04.50/0

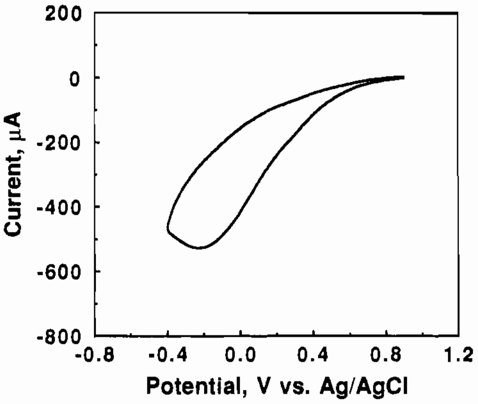


Figure 1. Cyclic voltammogram of 0.10 M $NaVO_3$ in 1.0 M H_2SO_4 at a 3.0 mm diameter glassy carbon electrode (scan rate, v = 0.10 V s^{-1}, T = 23 °C).

reoxidation. This irreversible behavior is analogous to regulatory enzymes which control metabolic flux *via* differential binding of substrate and product.[7a] Similar behavior has been reported for some electron-transfer enzymes.[7b]

Experimental Section

1. Reagents. Phosphomolybdic acid ($H_3PMo_{12}O_{40}$) and sodium metavanadate ($NaVO_3$) were obtained from Aldrich. Sulfuric acid was obtained from EM Science, $VOSO_4$ was obtained from Fisher, and D_2O was obtained from Cambridge Isotope Laboratories. All reagents were used as received. Electrochemical solutions contained 1.0 M H_2SO_4(aq) ≤0.10 M phosphomolybdic acid, and ≤0.10 M sodium metavanadate, with specific concentrations indicated in the relevant sections of the text. All solutions were deaerated with water-saturated N_2(g) for 5 min prior to use.

2. Physical Measurements. Cyclic voltammetric experiments were performed with an EG&G Model 273 potentiostat interfaced to an IBM compatible PC. Working electrodes for cyclic voltammetry were either a 3.0 mm diameter glassy carbon (Atomergic ChemMetals) disk or a 2.0 mm diameter Pt disk (Bioanalytical Systems). The geometric area of the working electrode was used in all calculations. A 2.0-cm^2 graphite cloth was the working electrode (National Electric Carbon, Grade WCA) for bulk electrolysis experiments. In all studies, Ag/AgCl was the reference electrode and a 1.0-cm^2 Pt foil served as the auxiliary electrode. Prior to use, glassy carbon and Pt working electrodes were polished with 0.3-μm α-Al_2O_3 (Buehler), washed thoroughly with deionized water, and then exposed to ultrasound for approximately 5 min. All potentials are reported versus a Ag/AgCl reference, unless otherwise specified.

^{31}P NMR spectra were recorded on a Varian 300, with all chemical shifts reported with respect to phosphoric acid. Solutions for ^{31}P NMR contained 10% D_2O. All spectra were re-recorded after the solutions were aged 1 month, and no significant changes in redox behavior or NMR shifts were observed after this time period.

Results

1. Vanadium-Substituted Phosphomolybdic Acid. The standard potential, $E_1°$, of the vanadate/vanadyl redox couple[8]

$$\mathrm{VO_2^+ + 2H^+ + e^-} \overset{E_1^\circ}{\rightleftharpoons} \mathrm{VO^{2+} + H_2O} \tag{1}$$

is +1.00 V vs NHE (+0.80 V vs Ag/AgCl).[9] However, as depicted in Figure 1, the overall reduction of VO_2^+(aq) to VO^{2+}, involving proton-, electron-, and oxygen-transfer steps, is irreversible in 1.0 M H_2SO_4(aq) under typical electrochemical conditions at a glassy carbon electrode. A diffusion-limited peak was not observed until $E < -0.10$ V, i.e., almost 1 V more negative than the standard potential of the redox couple. Addition of inert counterions such as 0.20 M $NaClO_4$ had negligible effect on the voltammetry. Similar irreversible electrochemical behavior, with only a slightly more positive potential for the diffusion-limited reduction peak ($E < +0.1$ V), was observed at a Pt working electrode.

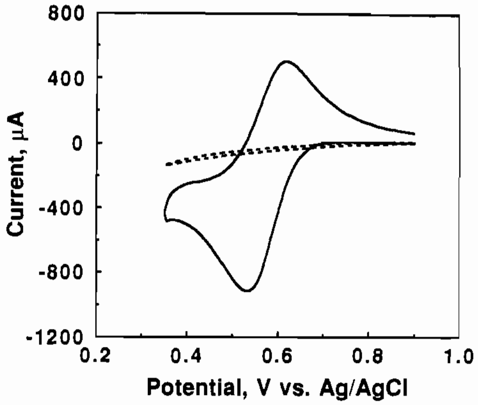


Figure 2. Cyclic voltammogram of 0.10 M $NaVO_3$ (- - -) and 0.10 M $NaVO_3$–0.10 M $H_3PMo_{12}O_{40}$ (—) in 1.0 M H_2SO_4 at a 3.0 mm diameter glassy carbon electrode (v = 0.10 V s^{-1}, T = 23 °C).

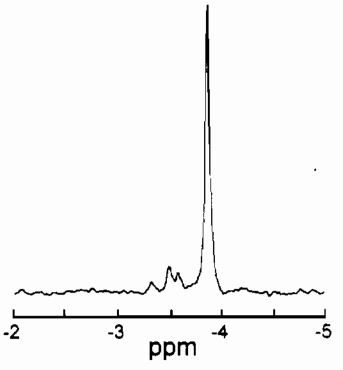


Figure 3. ^{31}P NMR spectrum of 0.10 M $NaVO_3$–0.10 M $H_3PMo_{12}O_{40}$ in 1.0 M H_2SO_4–10% D_2O (T = 23 °C), aged 1 month.

Addition of $PMo_{12}O_{40}^{3-}$ to the VO_2^+(aq) solution produced another electrochemically active species, ($PMo_{12-n}V_nO_{40}^{(3+n)-}$). For a 1:1 ratio of [$VO_2^+$]:[$PMo_{12}O_{40}^{3-}$], quasi-reversible electrochemical behavior (ΔE_p = 81 mV at 100 mV s^{-1}) was observed at a formal potential of $E_2°'$ = +0.55 V (Figure 2, eq 2). The formation of the $PMo_{11}VO_{40}^{4-}$ Keggin structure in these solutions was confirmed by ^{31}P NMR, which showed a prominent peak at δ = −3.8 ppm (Figure 3). This spectrum is in accord with prior spectra of the $PMo_{11}VO_{40}^{4-}$ complex.[3d] These 1:1 [VO_2^+(aq)]:[$PMo_{12}O_{40}^{3-}$] solutions displayed only small amounts of $PMo_{10}V_2O_{40}^{5-}$ (δ = −3.2 to −3.6 ppm) and contained negligible amounts of more highly substituted ($n > 2$) species (δ = −2 to −3 ppm).[3d] The observed electrochemical behavior is therefore attributable to the following oxidation state change of the $PMo_{11}VO_{40}^{4-}$ species:

$$\mathrm{PMo_{11}VO_{40}^{4-} + e^-} \overset{E_2^{\circ\prime}}{\rightleftharpoons} \mathrm{PMo_{11}VO_{40}^{5-}} \tag{2}$$

At pH = 0, the $PMo_{11}VO_{40}^{4-}$ and/or $PMo_{11}VO_{40}^{5-}$ species may be protonated, but all of our experiments were performed at constant pH, so this component of the reaction was of no concern in this work.

The $PMo_{11}VO_{40}^{4-}$ species should also, of course, be accessible through addition of VO_2^+(aq) to phosphomolybdic acid. Figure 4a shows the redox behavior of phosphomolybdic acid before and after addition of VO_2^+(aq). The cyclic voltammetry clearly shows that addition of VO_2^+(aq) resulted in incorporation of V^V into the polyoxoanion structure. In Figure 4a (dashed line), the first reduction wave corresponds to the reduction of V^V in the

---

(7) (a) Burbaum, J. J.; Raines, R. T.; Albery, W. J.; Knowles, J. R. *Biochemistry* **1989**, *28*, 9293–9305. (b) Sucheta, A.; Ackrell, B. A. C.; Cochran, B.; Armstrong, F. A. *Nature* **1992**, *356*, 361–362.

(8) Vanadium(V) was added in the form of sodium metavanadate ($NaVO_3$). At pH < 2, V(V) will exist in solution as VO_2^+.[9]

(9) Israel, Y.; Meites, L. *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Ed.; Marcel Dekker: New York, 1976; Vol. VII, Chapter 2.

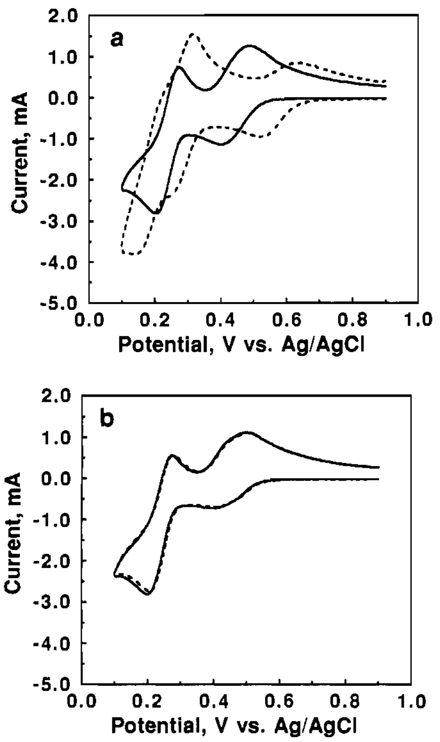


Figure 4. Effect of addition of (a) $NaVO_3$ and (b) $VOSO_4$ on cyclic voltammograms of 0.10 M $H_3PMo_{12}O_{40}$ in 1.0 M H_2SO_4 at a 3.0 mm diameter glassy carbon electrode (v = 0.10 V s^{-1}, T = 23 °C). [V]:[$H_3PMo_{12}O_{40}$]: 0:1 (—) 1:1 (- - -).

$PMo_{11}VO_{40}{}^{4-}$ cluster, while the second reduction wave arises from reduction of the Keggin cage.[10] The source of the third reduction has not been identified although it is likely due to further reduction of the Keggin cage. As shown in Figure 2, the approximately equal cathodic and anodic peak currents corresponding to reduction/oxidation of bound V^V indicate that the vanadium was not lost from the Keggin structure upon reduction during the time scale of these experiments.

In contrast, as depicted in Figure 4b, addition of $VO^{2+}(aq)$ did not affect the redox behavior of the polyoxoanion species. This shows that V^{IV} was not persistently incorporated into the polyoxoanion structure for at least three oxidation states of the heteropolyoxoanion species.

2. Electrocatalytic Reduction of $VO_2{}^+(aq)$. The cyclic voltammetric data of Figures 2 and 4 imply that phosphomolybdic acid will act as an electrocatalyst for reduction of $VO_2{}^+(aq)$, provided that either electron exchange or V exchange is facile between the aqueous and polyoxoanion-bound V species. As shown in Figure 5, addition of $VO_2{}^+(aq)$ in excess of 1:1 [$VO_2{}^+(aq)$]:[$PMo_{12}O_{40}{}^{3-}$] resulted in a catalytic current for the reduction of $VO_2{}^+(aq)$ to $VO^{2+}(aq)$. This behavior was observed at both glassy carbon and Pt working electrodes. As shown in Figure 6, the peak cathodic current at +0.50 V was directly proportional to [$VO_2{}^+$].

Bulk electrolysis experiments verified the electrocatalytic nature of the process, with electrolysis of a solution containing 1.70 mmol of $VO_2{}^+(aq)$ in the presence of 0.20 mmol of $PMo_{12}O_{40}{}^{3-}$ producing 160 C at +0.35 V. In contrast, reoxidation of this solution at +0.90 V only yielded 19 C. The 160 C corresponded to the value expected for the reduction of the V bound in the catalyst and the free $VO_2{}^+(aq)$, while the 19 C corresponded only to the reoxidation of the V bound in the heteropolyoxometalate catalyst, with negligible reoxidation of the free $VO^{2+}(aq)$. The heteropolyoxometalate therefore acted as a catalyst for the reduction of free $VO_2{}^+(aq)$ but did not effectively catalyze the reoxidation of free $VO^{2+}(aq)$.

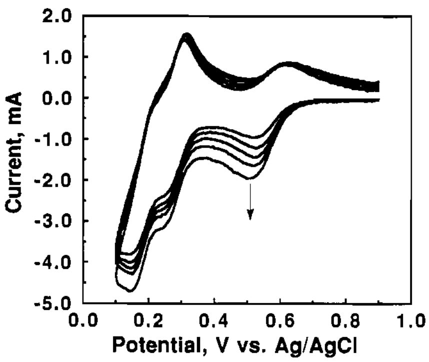


Figure 5. Effect of addition of $NaVO_3$ ([$VO_2{}^+$]:[$H_3PMo_{12}O_{40}$] from 1:1 to 2:1) on cyclic voltammograms of 0.10 M $H_3PMo_{12}O_{40}$ in 1.0 M H_2SO_4 at a 3.0 mm diameter glassy carbon electrode (v = 0.10 V s^{-1}, T = 23 °C). Arrow indicates the effect of increasing [$VO_2{}^+$].

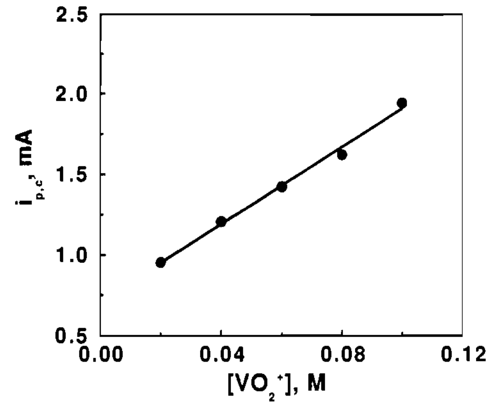


Figure 6. Plot of $i_{p,c}$ *vs* [$VO_2{}^+$]. See Figure 5 for experimental conditions.

Reoxidation of the vanadium inside the Keggin structure in the presence of excess $VO_2{}^+(aq)$ may occur either by replacement of bound, reduced V or by electron or atom transfer from the reduced complex to $VO_2{}^+(aq)$. For both pathways, the overall reaction sequence can be written as

$$PMo_{12-n}V_nO_{40}{}^{(3+n)-} + e^- \overset{E_{3a}{}^{\circ\prime}}{\rightleftharpoons} PMo_{12-n}V_nO_{40}{}^{(4+n)-} \quad (3a)$$

$$PMo_{12-n}V_nO_{40}{}^{(4+n)-} + 2H^+ + VO_2{}^+ \underset{k_{-3}}{\overset{k_{+3}}{\rightleftharpoons}} PMo_{12-n}V_nO_{40}{}^{(3+n)-} + H_2O + VO^{2+} \quad (3b)$$

where the net reaction is shown in eq 1. Regardless of whether proton transfer accompanies the electron transfer or occurs in a subsequent step, the basic reaction sequence of eq 3 is a classic EC′ electrocatalytic process[11] in which an electron-transfer step (eq 3a), E, is followed by a catalytic chemical step, C′, that regenerates the original electroactive species (eq 3b). In the EC′ mechanism, the catalyst is electroactive whereas the substrate is

---

[10] The second reduction wave in Figure 4a shifts ca. +50 mV while its magnitude remains constant with addition of $VO_2{}^+$ to $PMo_{12}O_{40}{}^{3-}$ up to a 1:1 ratio, thereby supporting the suggestion that this wave is associated with the reduction of the Keggin cage.

[11] (a) Savéant, J.-M.; Vianello, E. *Electrochim. Acta* **1963**, *8*, 905–923. (b) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706–723. (c) Savéant, J.-M.; Vianello, E. *Electrochim. Acta* **1967**, *12*, 629–646. (d) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Savéant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *113*, 19–40.

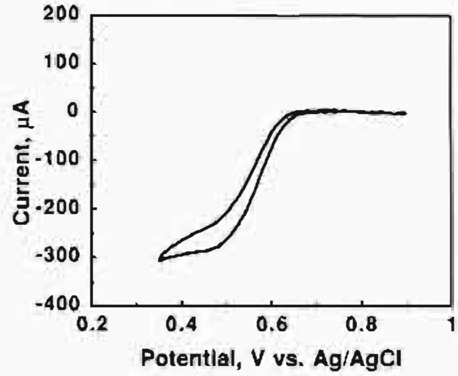


Figure 7. Cyclic voltammogram of 0.10 M $NaVO_3$–0.010 M $H_3PMo_{12}O_{40}$ in 1.0 M H_2SO_4 at a 3.0 mm diameter glassy carbon electrode after background subtraction (v = 0.10 V s^{-1}, T = 23 °C).

electrochemically inert. Under our conditions, due to the sluggish electrochemical kinetics of VO_2^+(aq) and VO^{2+}(aq) at glassy carbon surfaces, free VO_2^+(aq) and free VO^{2+}(aq) can be considered electrochemically inert over our potential range.

When the catalytic reaction (eq 3b) controls the overall reaction rate, theory for an EC′ reaction sequence predicts that the diffusion-limited catalytic current will be directly proportional to the concentration of the electrochemically inert substrate (i.e. VO_2^+ in eq 3b). This was observed in a plot of $i_{p,c}$ *vs* [VO_2^+] (Figure 6).

In addition, with the appropriate conditions (i.e. low catalyst concentration), the chemical step in the EC′ reaction can be made to be the rate-determining step. If the chemical reaction step is irreversible (i.e. $k_{+3} >> k_{-3}$), a steady-state voltammetric response will be produced in which the limiting current (i_∞) is independent of the time scale of the experiment. Under these conditions, the limiting current is directly related to the rate of the chemical reaction step[11] (eq 3b), with

$$i_\infty = nFAC_{Ox}^*(D_{Ox}k'C_V^*)^{1/2} \qquad (4)$$

In this equation, n represents the number of electrons transferred (1), F is Faraday's constant (96485 C mol^{-1}), A is the electrode area (cm^2), C_{Ox}^* is the bulk concentration (mol cm^{-3}) of the electroactive species ($PMo_{12-n}V_nO_{40}^{(3+n)-}$), D_{Ox} is the diffusion coefficient (cm^2 s^{-1}) of the electroactive species ($PMo_{12-n}V_nO_{40}^{(3+n)-}$), k' is a second-order rate constant (M^{-1} s^{-1}) for the forward catalytic reaction (which in our case is k_{+3}, a pseudo-second-order rate constant that is also implicitly dependent on [H^+]), and C_V^* is the bulk concentration of the electroinactive species, [VO_2^+(aq)].

In accord with theoretical expectations, a [VO_2^+(aq)]:[$PMo_{12}O_{40}^{3-}$] ratio of 10:1 produced a steady-state catalytic response that was independent of scan rate (Figure 7). The rate constant for reaction 3b was obtained from the limiting current under these conditions (i_∞ = 300 µA at +0.40 V, after subtracting the background current). Using values of $C_{Ox}^* = 1.0 \times 10^{-5}$ mol cm^{-3}, A = 0.071 cm^2, $D_{Ox} = 6.0 \times 10^{-6}$ cm^2 s^{-1},[12] and $C_V^* = 1.0 \times 10^{-4}$ mol cm^{-3} yields a value for a second-order rate constant, k', of 33 M^{-1} s^{-1}, which corresponds to a turnover number of 3.3×10^3 s^{-1}. Using this value of k' under the experimental conditions of Figure 5 (i.e. [VO_2^+(aq)]:[$PMo_{12}O_{40}^{3-}$] = 2:1), theory predicts that the peak catalytic current should be 200% of the peak current[11d] obtained for reduction of $PMo_{11}VO_{40}^{4-}$ in the absence of excess VO_2^+(aq) (i.e. when [VO_2^+(aq)]:[$PMo_{12}O_{40}^{3-}$] = 1:1). This is consistent with the data in Figure 5, where the peak current at +0.50 V increased by a factor of 2 (i.e. from –0.90 to –1.90 mA) when the [VO_2^+(aq)]:[$PMo_{12}O_{40}^{3-}$] ratio increased from 1:1 to 2:1.

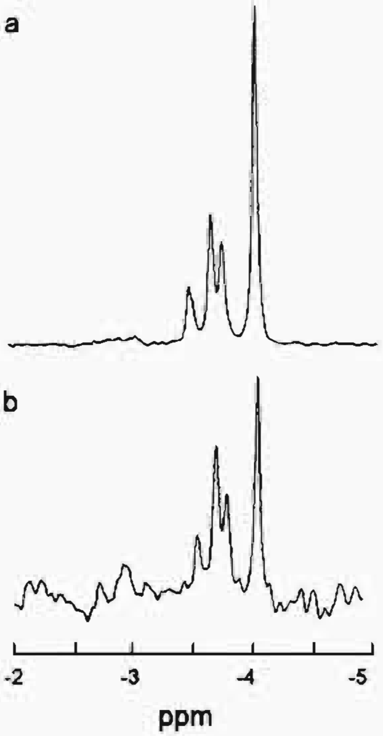
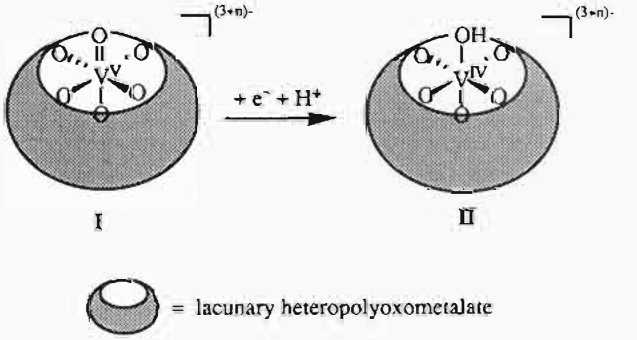


Figure 8. ^{31}P NMR of (a) 0.20 M $NaVO_3$–0.10 M $H_3PMo_{12}O_{40}$ and (b) 0.10 M $NaVO_3$/0.010 M $H_3PMo_{12}O_{40}$ in 1.0 M H_2SO_4–10% D_2O (T = 23 °C), aged 1 month.

Scheme 1



Discussion

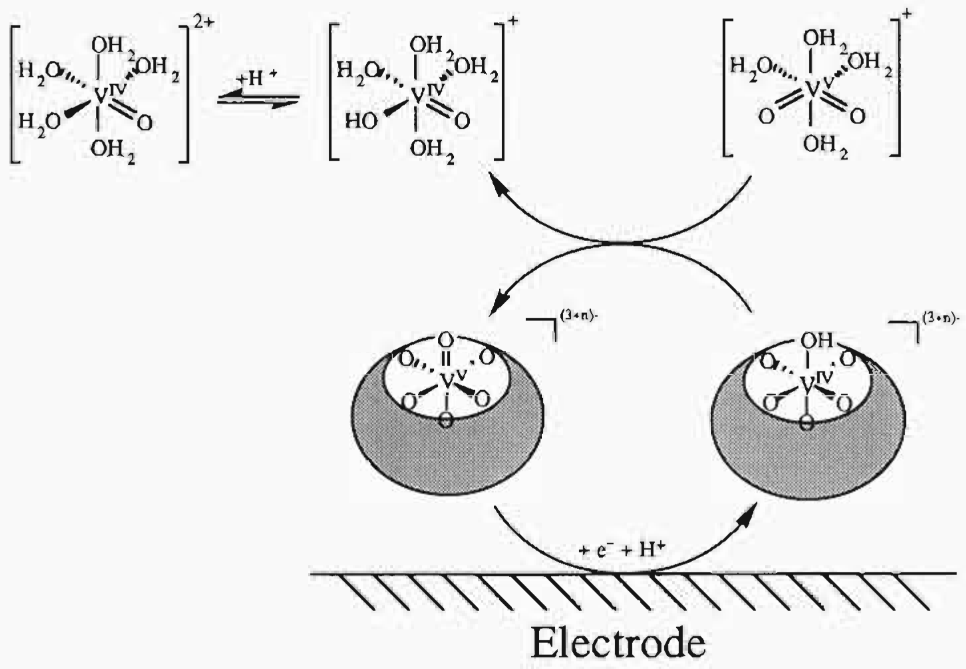
The electrochemical data presented above clearly demonstrate that, under our conditions, phosphomolybdic acid is an effective electrocatalyst for the reduction of VO_2^+(aq) to VO^{2+}(aq). However, addition of $PMo_{12}O_{40}^{3-}$ to 1.0 M H_2SO_4(aq)–VO_2^+(aq)–VO^{2+}(aq) solutions does not allow the electrocatalytic oxidation of VO^{2+}(aq) to VO_2^+(aq). This somewhat unusual behavior arises because the $PMo_{12}O_{40}^{3-}$ anion reacts with VO_2^+(aq) to yield the electroactive species $PMo_{11}VO_{40}^{4-}$, whose formal potential is ≈0.3 V more negative than the VO_2^+(aq)/VO^{2+}(aq) standard potential (Figure 2). The reduced form of this species, $PMo_{11}VO_{40}^{5-}$, is therefore thermodynamically capable of effecting the reduction of VO_2^+(aq), whereas VO^{2+}(aq) cannot be oxidized by $PMo_{11}VO_{40}^{4-}$. This reaction sequence is supported by ^{31}P NMR and cyclic voltammetric data (Figures 2 and 3), which confirm the formation of $PMo_{11}VO_{40}^{4-}$ in solutions with equal concentrations of $PMo_{12}O_{40}^{3-}$ and V^V.

As suggested in eq 3, many different species, each having different ratios of vanadium to molybdenum, may be present in acidic solutions containing V and $PMo_{12}O_{40}^{3-}$. The stoichiometry and speciation of the phosphovanadomolybdate clusters will, of course, depend on the solution conditions.[1-3] Under both stoichiometric (0.10 M VO_2^+–0.10 M $H_3PMo_{12}O_{40}$ in 1.0 M H_2SO_4(aq)) and electrocatalytic (0.20 M VO_2^+–0.10 M

---

[12] Baker, L. C. W.; Pope, M. T. *J. Am. Chem. Soc.* **1960**, *82*, 4176–4179.

Scheme 2



$H_3PMo_{12}O_{40}$ in 1.0 M H_2SO_4(aq)) conditions, ^{31}P NMR spectra showed that the dominant species in solution were $PMo_{11}VO_{40}^{4-}$ and $PMo_{10}V_2O_{40}^{5-}$ (n = 1 and 2) (Figures 3 and 8a).[3d] These species remained dominant as the concentration of phosphomolybdic acid was decreased from 0.10 to 0.010 M in the presence of 0.10 M VO_2^+ (Figure 8b). These data therefore support the reaction sequence presented in eq 3 for the overall electrocatalytic process.

Regeneration of V^V in the reduced heteropolyoxometalate may occur either by displacement of bound V^{IV} by free VO_2^+(aq) or by direct electron transfer from the reduced polyoxoanion to VO_2^+(aq). Evidence for direct electron transfer between $PMo_{11}V^{IV}O_{40}^{5-}$ and VO_2^+(aq) was obtained through the use of quinone/hydroquinone and phosphotungstic acid in place of $PMo_{11}V^VO_{40}^{4-}$/$PMo_{11}V^{IV}O_{40}^{5-}$. With quinone/hydroquinone as the catalytic redox couple, an irreversible electrocatalytic reduction of VO_2^+(aq) was observed, with the catalytic current for the V reduction occurring at the quinone/hydroquinone redox potential ($E_{p,c}$ = +0.32 V vs Ag/AgCl). In related experiments using $PW_{12}O_{40}^{3-}$, an irreversible electrocatalytic reduction of VO_2^+(aq) was observed at $E_{p,c}$ = +0.00 V. This electrocatalytic reduction occurred at the first reduction potential of $PW_{12}O_{40}^{3-}$. Furthermore, unlike $PMo_{12}O_{40}^{3-}$, $PW_{12}O_{40}^{3-}$ did not yield electrochemical evidence for significant V^V binding. This indicates that the reduced Keggin cage, without significant binding of V, can act as an electrocatalyst for VO_2^+(aq) reduction. These results therefore suggest that direct electron transfer, mediated by the catalytic species, is a facile kinetic pathway for the electrocatalytic reduction of VO_2^+(aq) to VO^{2+}(aq).

Although our electrochemical and NMR data do not provide structural information on the reduced phosphomolybdic acid complex, the observed reaction chemistry is consistent with prior suggestions of inner-sphere, proton-coupled electron transfer in the oxidation of hydroquinones by metal oxo species such as $[(bpy)_2(py)Ru^{IV}(O)]^{2+}$.[13] The reversible redox behavior of heteropolyoxometalates has been associated with the terminal oxo groups present in type I polyoxoanions.[14] Reduction of such complexes under acidic conditions ($1e^-/1H^+$) may result in hydroxo groups similar to the reduction of quinone to hydroquinone[15] and the reduction of $[(bpy)_2(py)Ru^{IV}(O)]^{2+}$ to $[(bpy)_2(py)Ru^{III}(OH)]^{2+}$ [13] or protonation of bridging oxygens. As illustrated in Scheme 1, reduction of the oxo–V^V-substituted polyoxoanion (**I**) may produce the hydroxo–V^{IV}-substituted polyoxoanion, **II**. This anion would presumably be stabilized by the acceptor properties of the polyoxoanion. Species **II** may then allow a pathway for inner-sphere, proton-coupled electron transfer (i.e. a concerted electron/proton transfer), by analogy to the Ru^{IV}–oxo system. This would result in the overall electrocatalytic reaction illustrated in Scheme 2. Of course, alternate mechanisms, including outer-sphere electron transfer and V atom exchange, are also possible and cannot be distinguished from the available data.

The shift in formal potential of the VO_2^+/VO^{2+}(aq) redox couple upon incorporation of V into the Keggin structure (Figures 2 and 4) indicates preferential incorporation of V^V (i.e. $K_3 >> 1$ in eq 3b) into the polyoxoanion framework. Under conditions where the electrochemical step is Nernstian and the equilibrium of the following chemical step is fast, a value for K_3 can be determined from the cyclic voltammetric data (assuming n = 1). The Nernst relationship for the reaction in eq 1 can be written as

$$E = E_1{}^\circ + \frac{RT}{F}\ln\frac{(VO_2^+)(H^+)^2}{(VO^{2+})(H_2O)} \qquad (5)$$

where $E_1{}^\circ$ is the standard potential (+0.80 V)[9] of the free VO_2^+(aq)/VO^{2+}(aq) redox couple. Considering the equilibrium of the catalytic step shown in eq 3b

$$K_3 = \frac{k_{+3}}{k_{-3}} = \frac{[PMo_{11}VO_{40}^{4-}][VO^{2+}][H_2O]}{[PMo_{11}VO_{40}^{5-}][VO_2^+][H^+]^2} \qquad (6)$$

and substituting eq 6 into eq 5, the measured potential can be expressed as

---

[13] (a) Wells, C. F.; Kuritsyn, L. V. *J. Chem. Soc. A* **1970**, 1372–1376. (b) Binstead, R. A.; McGuire, M. E.; Dovletoglou, A.; Seok, W. K.; Roecker, L. E.; Meyer, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 173–186.

[14] Reference 1b, Chapter 6.

[15] (a) Laviron, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *164*, 29–46. (b) Laviron, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *208*, 357–372.

$$E = E_1° + \frac{RT}{F}\ln\frac{[PMo_{11}VO_{40}{}^{4-}]}{[PMo_{11}VO_{40}{}^{5-}]} - \frac{RT}{F}\ln K_3 \qquad (7)$$

Since the Nernst relationship for the electrochemical step (eq 3a) is

$$E = E_{3a}° + \frac{RT}{F}\ln\frac{[PMo_{11}VO_{40}{}^{4-}]}{[PMo_{11}VO_{40}{}^{5-}]} \qquad (8)$$

combining eq 7 and 8 yields

$$K_3 = e^{(F/RT)(E_1° - E_{3a}°)} \qquad (9)$$

Using the reported value of $E_1° = +0.80$ V and taking the formal potential obtained in this study, $E_{3a}°' = +0.55$, as an approximation of the standard potential, $E_{3a}°$,[16] yields $K_3 = 1.7 \times 10^4$ M^{-1}.[17] The negative shift in the formal potential of the $VO_2{}^+$/VO^{2+} couple is a direct result of the shift in the equilibrium favoring incorporation of V^V into the Keggin structure. The enhanced stability of V^V relative to V^{IV} is consistent with the preference of V^{IV} for square pyramidal coordination,[5c] while the Keggin structure imposes a distorted octahedral geometry on bound metal ions.[6] This shift in redox potential precludes the electrocatalytic oxidation of VO^{2+}(aq) by the electrocatalytic species but provides a substantial driving force for the reduction of $VO_2{}^+$(aq). The overall electrochemical behavior of this system, including the cyclic voltammetry and electrocatalytic properties, can thus be understood in a self-consistent fashion.

In summary, the electrocatalytic behavior of phosphomolybdic acid in acidic $VO_2{}^+$(aq) solutions is similar to enzyme-like behavior involving differential binding of substrate relative to product.[7a] This leads to the electrocatalytic reduction of $VO_2{}^+$(aq) to VO^{2+}(aq) without efficient electrocatalysis of the reverse reaction. This behavior can be understood from the thermodynamic and kinetic properties of the cluster species that are formed in solutions containing $PMo_{12}O_{40}{}^{3-}$ and excess $VO_2{}^+$(aq). In this system, as is the case for regulatory enzymes, free energy is sacrificed for control over the flux of reaction products.

Acknowledgment. We acknowledge ARPA for support of this work and thank Professors F. C. Anson and J. E. Bercaw and Dr. J. Labinger of Caltech for helpful discussions and Dr. D. A. Keire for help with ^{31}P NMR. We also acknowledge Dr. J. Grate for generously supplying a preprint of ref 3d.

---

(16) On the basis of the known value of $pK_{a2} = 1.92$ for H_2SO_4(aq), $[H^+]$ for a 1.0 M H_2SO_4 solution was calculated to be 1.02 M. Therefore the activity of protons was approximated to be unity under these conditions for the purpose of calculating the standard potential of the V species.

(17) Although K_3 is unitless as defined by eq 6, it can be reported in units of M^{-1} since, under the standard convention, the H_2O concentration is incorporated implicitly into K_3.