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Photoinitiated Two-Electron Oxidation of Tris(1,10-phenanthroline)vanadium(II)

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The redox and photochemical properties of vanadium polypyridine complexes have been combined to achieve the first example of photoredox-initiated two-electron oxidation at a single transition-metal center. Cyclic voltammetry of $V(phen)_3^{2+}$ (phen = 1,10-phenanthroline) in CH_2Cl_2 shows three reversible redox couples due to $V(phen)_3^{3+/2+}$, $V(phen)_3^{2+/+}$, and $V(phen)_3^{+/0}$, with half-wave potentials of 0.09, −1.51, and −1.70 V, respectively, vs. Fc/Fc^+ (Fc = ferrocene). Solutions of the vanadium(III) complex $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ in CH_3CN exhibit a single irreversible oxidation wave, which is probably associated with formation of a mononuclear vanadium(IV) complex. This electrogenerated vanadium(IV) species is also electroactive, showing quasi-reversible oxidation and reduction waves. Similar quasi-reversible waves observed in the $V(phen)_3^{2+}$ voltammograms are attributable to the same species, formed by hydrolysis of $V(phen)_3^{3+}$ and subsequent rapid oxidation. In buffered aqueous solutions (pH ≥8), $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ spontaneously reduces the electron acceptors MV^{2+} (methylviologen or 1,1′-dimethyl-4,4′-bipyridinium) and $Fe(CN)_6^{3-}$. The vanadium-containing electron-transfer product is a VO^{2+} complex, as identified by its ESR spectrum. Thus, irradiation of a solution (pH 8) of $V(phen)_3^{2+}$ and MV^{2+} ($\lambda > 500$ nm) leads to the one-electron photooxidation of $V(phen)_3^{2+}$, followed by thermal electron transfer to produce VO^{2+}.

Introduction

We have recently been investigating the photophysics and photochemistry of $V(NN)_3^{2+}$ (NN = polypyridine) complexes.[1,2] They offer two advantages over other photoredox-active metal complexes. First, they absorb intensely in the 500–900-nm region. This allows for photochemical reactions driven by light of significantly lower energy than is required with species such as $Ru(NN)_3^{2+}$[3] or $Cr(NN)_3^{3+}$.[4-6] Second, the availability of a broad range of vanadium oxidation states[7] should make photoinitiated multielectron-transfer reactions possible. We have previously demonstrated[1] that photooxidation of $V(NN)_3^{2+}$ in unbuffered solutions results in permanent formation of the vanadium(III) dimer $[(NN)_2V(\mu\text{-}OH)_2V(NN)_2]^{4+}$. This is the first system in which the undesirable electron-back-transfer reaction, which ordinarily follows the primary photoredox process, has been inhibited by the formation of a stable dimeric species. We have now studied the mechanism of this irreversible photooxidation by electrochemical methods. We have also found that the initial photooxidation product, $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$, can be oxidized further in more basic solutions, and we have combined the two processes to achieve the net two-electron photochemical transformation of $V(phen)_3^{2+}$ to VO^{2+}. These results represent the first example of photoinitiated two-electron oxidation at a single metal center.

Experimental Section

Materials. Vanadium trichloride (Aldrich) and 1,10-phenanthroline (Aldrich, Gold Label) were used without further purification, and ferrocene (Sigma) was purified by recrystallization from ethanol. For electrochemical studies spectrophotometric grade CH_2Cl_2 (MCB) and CH_3CN (Aldrich, Gold Label) were used. Literature procedures were used to prepare tetrabutylammonium trifluoromethanesulfonate, $(Bu_4N)(O_3SCF_3)$,[8] and $[V(phen)_3](O_3SCF_3)_2 \cdot H_2O$.[1] All other chemicals and solvents were reagent grade and were used as received.

$[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]Cl_4$. The synthesis of the vanadium(III) dimer was carried out under argon in a Schlenk apparatus. Vanadium trichloride (0.1 g, 0.64 mmol) was added to a solution of 1,10-phenanthroline (0.23 g, 1.27 mmol) in 5 mL of degassed aqueous ethanol (1:4 H_2O/EtOH). The solution immediately turned deep purple. It was stirred overnight and then filtered into a large excess of degassed acetone to give a dark purple microcrystalline product, which was collected and dried in vacuo. The electronic absorption spectrum of $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]Cl_4$ in water is shown in Figure 1. Absorption maxima are at 630 nm ($\epsilon = 5.2 \times 10^3$ M^{-1} cm^{-1}) and 530 nm ($\epsilon = 4.8 \times 10^3$ M^{-1} cm^{-1}). Anal. Calcd for $C_{48}H_{34}Cl_4N_8O_2V_2$: C, 57.72; H, 3.41; N, 11.22; Cl, 14.23. Found: C, 57.38; H, 3.36; N, 11.17; Cl, 14.02.

Procedures. For spectroscopic and photochemical measurements, samples were prepared by freeze–pump–thaw methods on a high-vacuum line. Electronic absorption spectra were recorded on a Cary 219 spectrophotometer. ESR measurements were made on a Century Series E-Line spectrometer with the use of degassed aqueous solutions in borosilicate glass capillaries.

Cyclic voltammetric measurements were made with a PAR Model 174A polarographic analyzer. The electrochemical cell utilized Pt-disk working and Pt-wire auxiliary electrodes and a Ag/AgCl (3 M aqueous NaCl) reference electrode. The half-wave potential of the Fc/Fc^+ (Fc = ferrocene) reference redox couple under our conditions was 0.43 V (in CH_3CN) or 0.54 V (in CH_2Cl_2). The electrolyte solution (0.1 M $(Bu_4N)(O_3SCF_3)$ in CH_3CN or CH_2Cl_2) was degassed by bubbling with purified Ar or N_2 for $^1/_2$ h. The appropriate vanadium complex was added and the voltammogram recorded immediately.

Results

Electrochemistry of $V(phen)_3^{2+}$. Our previous experiments with $V(phen)_3^{2+}$ in CH_3CN[1] showed a quasi-reversible one-electron redox couple at positive potentials and a very poorly resolved cathodic wave at negative potentials. However, in CH_2Cl_2, the cyclic voltammograms are considerably better resolved (Figure 2). The reversible wave at positive potentials ($E_{1/2} = 0.63$ V vs. Ag/AgCl) is assigned to $V(phen)_3^{3+/2+}$, and the two other closely spaced one-electron reversible waves are assigned to $V(phen)_3^{2+/+}$ and $V(phen)_3^{+/0}$ ($E_{1/2} = -0.97$ and −1.16 V, respectively). These potentials are comparable to those found by Saji and Aoyagui[9,10] for $V(bpy)_3^{2+/+}$ and $V(bpy)_3^{+/0}$ in DMF, but our voltammograms are more clearly resolved.

In addition to these waves, small quasi-reversible cathodic and anodic waves are also observed between 0 and −0.50 V. These waves are observed only if the electrode is first brought to potentials sufficiently positive to oxidize $V(phen)_3^{2+}$ to $V(phen)_3^{3+}$ (see dotted line in Figure 2). They are similar to waves seen in cyclic voltammograms of $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ (see below) and $VO(phen)_2^{2+}$.[11] The amplitude of the quasi-reversible waves increases, at the expense of the cathodic wave corresponding to reduction of $V(phen)_3^{3+}$ to $V(phen)_3^{2+}$, if bases such as pyridine

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(11) Salts of $VO(phen)_2^{2+}$ are only slightly soluble in CH_3CN, so that a direct comparison with our results for $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ is difficult. However, similar features are observed with $VO(phen)_2^{2+}$: a poorly resolved anodic wave at 1.0 V with a small return wave and a cathodic wave at −0.5 V with a corresponding anodic wave at −0.1 V. Rest potential measurements (−0.27 V) under these conditions indicate that the cathodic waves at −0.5 and +1.0 V are due to reduction and oxidation of $VO(phen)_2^{2+}$ respectively.

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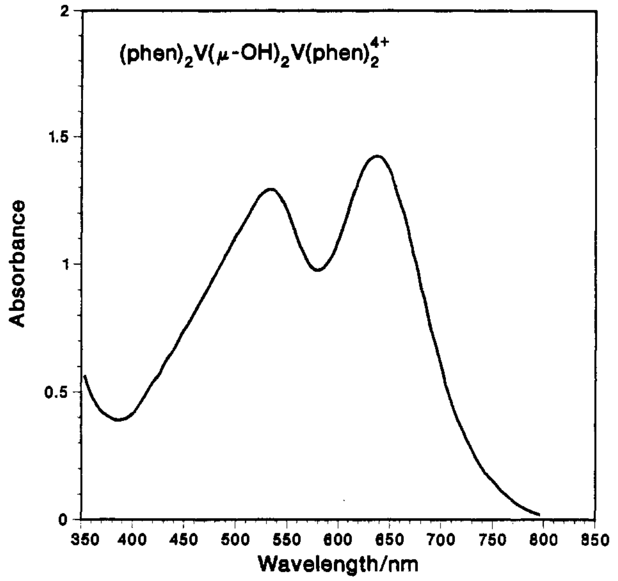

Figure 1. Electronic absorption spectrum of [(phen)$_2$V(μ-OH)$_2$V(phen)$_2$]Cl$_4$ in water.

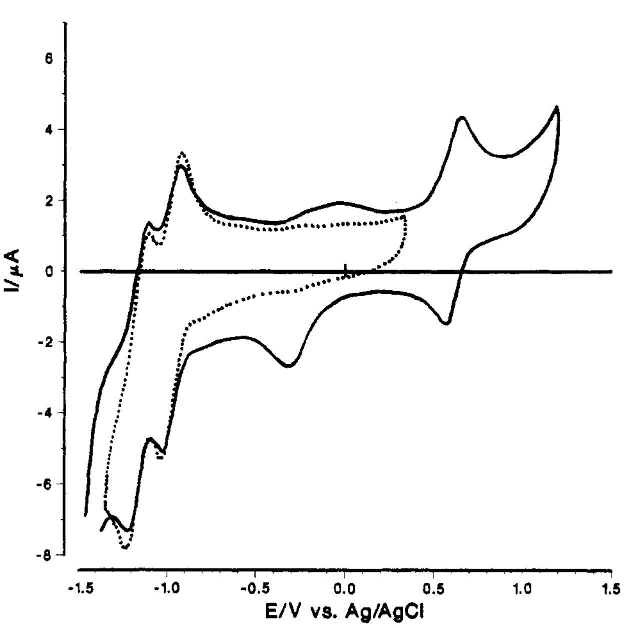

Figure 2. Cyclic voltammograms of [V(phen)$_3$](O$_3$SCF$_3$)$_2$ in CH$_2$Cl$_2$ (scan rate 500 mV s^{-1}). Anodic scan limit: 1.2 V (solid line); 0.35 V (dotted line).

or phenanthroline are added to the electrolyte solution (compare solid and dotted lines in Figure 3). Saturation of the V(phen)$_3^{2+}$ solution with degassed water, on the other hand, does not affect the voltammogram.

Electrochemistry of [(phen)$_2$V(μ-OH)$_2$V(phen)$_2$]Cl$_4$. Cyclic voltammetry performed on [(phen)$_2$V(μ-OH)$_2$V(phen)$_2$]Cl$_4$ in CH$_3$CN reveals a number of anodic and cathodic waves (Figure 4). The rest potential of the system is 0.12 V; therefore, the anodic wave at 0.60 V (marked A in Figure 4) is attributable to oxidation of [(phen)$_2$V(μ-OH)$_2$V(phen)$_2$]$^{4+}$. This oxidation is irreversible: no corresponding cathodic wave is observed even if the scan direction is reversed immediately after wave A (see dotted line in Figure 4). Waves D and E do not appear unless [(phen)$_2$V(μ-OH)$_2$V(phen)$_2$]$^{4+}$ is first oxidized, at ca. 0.7 V (see dashed line in Figure 4). They are also similar to those exhibited by solutions of the "vanadyl" (vanadium(IV)) complex VO(phen)$_2^{2+}$.[11] We therefore assign wave D to reduction of an electrogenerated vanadyl complex, probably VO(phen)$_2^{2+}$, and wave E to the reoxidation of the resulting mononuclear vanadium(III) species.

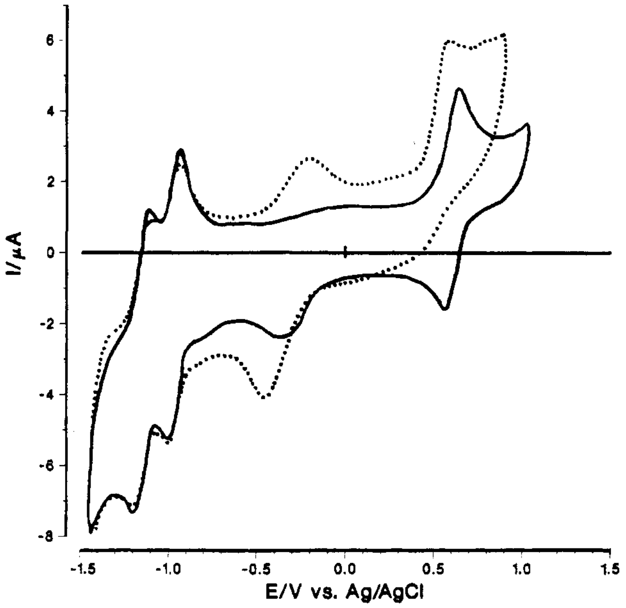

Figure 3. Cyclic voltammograms of [V(phen)$_3$](O$_3$SCF$_3$)$_2$ in CH$_2$Cl$_2$ (scan rate 500 mV s^{-1}), before (solid line) and after (dotted line) addition of pyridine to the electrolyte solution.

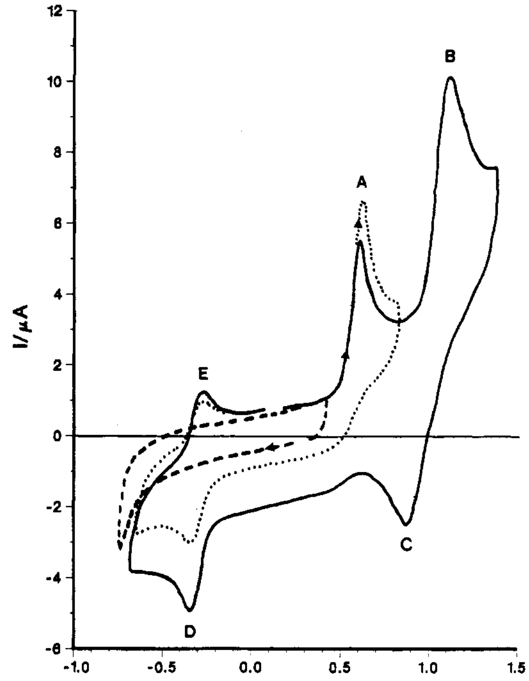

Figure 4. Cyclic voltammograms of [(phen)$_2$V(μ-OH)$_2$V(phen)$_2$]Cl$_4$ in CH$_3$CN (scan rate 500 mV s^{-1}): solid line, initial anodic scan; dotted line, anodic scan, but with scan direction reversed at 0.8 V; dashed line, initial cathodic scan. Assignments: A, oxidation of [(phen)$_2$V(μ-OH)$_2$V(phen)$_2$]$^{4+}$; B, oxidation of VO(phen)$_2^{2+}$; C, reduction of vanadium(V); D, reduction of VO(phen)$_2^{2+}$; E, oxidation of mononuclear vanadium(III). See text for details.

The remaining features in Figure 4 (waves B and C) are likely to be associated with a vanadium(IV)/vanadium(V) couple. Again, similar anodic and cathodic waves were observed with VO(phen)$_2^{2+}$.[11]

None of the waves in Figure 4 is attributable to Cl$^-$: addition of solid tetramethylammonium chloride to the solutions results in the appearance of new waves at 1.29 (oxidation) and 0.68 V (reduction). Cyclic voltammograms for [(phen)$_2$V(μ-OH)$_2$V(phen)$_2$]Cl$_4$ in CH$_2$Cl$_2$ are similar to those shown in Figure 4, except that the background current at potentials above ca. 0.7 V is much larger. As a result, only waves corresponding to A, D, and E can be seen in CH$_2$Cl$_2$ solutions.

Chemical Oxidation of [(phen)$_2$V(μ-OH)$_2$V(phen)$_2$]$^{4+}$. In our previous work, we showed that photoinduced electron transfer from

$V(phen)_3^{2+}$ to various electron acceptors leads to the stable vanadium(III) species $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$.[1] To investigate the possibility of a second thermal electron-transfer reaction of $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$, we examined mixtures of $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ with electron acceptors in the dark in aqueous solutions of known pH. With methylviologen (1,1′-dimethyl-4,4′-bipyridinium, MV^{2+}) as acceptor, no reaction was observed at pH 1.0 (0.1 M HCl) or 7.0 (phosphate or acetate buffers). However, at pH 8.0 (tris buffer; tris = tris(hydroxymethyl)aminomethane) $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ and MV^{2+} reacted immediately to form MV^+, as confirmed by its characteristic absorption spectrum (maxima at 395 and 605 nm).[12,13] Although the vanadium-containing product gave no detectable electronic absorption bands, the reaction mixture showed an intense 8-line ESR spectrum[14] characteristic of VO^{2+}. Thus, the overall reaction is

$$[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+} + 2MV^{2+} \rightarrow 2VO^{2+} + 2MV^+ + 2H^+ + 4phen \quad (1)$$

Other oxidants also react with $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ at pH 8. Solutions of orange $Fe(CN)_6^{3-}$,[15] for example, and violet $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ are both decolorized on mixing, as is expected for the following reaction:

$$[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+} + 2Fe(CN)_6^{3-} \rightarrow 2VO^{2+} + 4phen + 2Fe(CN)_6^{4-} + 2H^+ \quad (2)$$

Photoinitiated Two-Electron Oxidation. Samples containing $V(phen)_3^{2+}$ and MV^{2+} in tris buffer (pH 8.0) give no ESR signals if kept in the dark. However, irradiation of the solutions ($\lambda >$ 500 nm) leads to the formation of blue MV^+ and also the development of the 8-line VO^{2+} ESR spectrum. In contrast to our previous photoredox results in unbuffered solutions,[1] therefore, photooxidation of $V(phen)_3^{2+}$ at pH 8 yields the two-electron-transfer product VO^{2+}.

Discussion

Formation of $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ from $V(phen)_3^{2+}$. One-electron oxidation of $V(phen)_3^{2+}$ is followed by hydrolysis and dimerization of $V(phen)_3^{3+}$ to yield $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$. This conversion was first studied by Bennett and Taube[16] via thermal oxidation of $V(phen)_3^{2+}$. We have recently shown that it can be accomplished photochemically as well, using electron acceptors (represented by A in eq 4 and 5).[1] The photooxidation proceeds via the quartet metal-to-ligand charge-transfer (^{4}MLCT) excited state of $V(NN)_3^{2+}$.[2]

$$V(phen)_3^{2+}(^4A_2) \xrightarrow{h\nu} V(phen)_3^{2+}(^4MLCT) \quad (3)$$

$$V(phen)_3^{2+}(^4MLCT) + A \rightarrow V(phen)_3^{3+} + A^- \quad (4)$$

$$2V(phen)_3^{3+} + 2H_2O \rightarrow [(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+} + 2phen + 2H^+ \quad (5)$$

Our electrochemical studies of $V(phen)_3^{2+}$, which show reversible waves connecting the 0, I, II, and III oxidation states, also reveal anodic and cathodic waves closely analogous to those exhibited by solutions of $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ and $VO(phen)_2^{2+}$. These new waves yield additional information concerning the transformation represented by eq 3–5. The mechanism of reaction 5 is of special interest because it provides a substantial barrier toward electron back-transfer from A^- to vanadium(III), thereby rendering the photoredox process irreversible. Since $V(phen)_3^{3+}$ (d^2) is expected to be more labile toward substitution than $V(phen)_3^{2+}$,[17] reaction 5 probably occurs by initial aquation. A likely intermediate in the process is $V(phen)_2(H_2O)_2^{3+}$:

$$V(phen)_3^{3+} + 2H_2O \rightarrow V(phen)_2(H_2O)_2^{3+} + phen \quad (6)$$

$$2V(phen)_2(H_2O)_2^{3+} + 2B \rightarrow [(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+} + 2H_2O + 2BH^+ \quad (7)$$

Our electrochemical measurements show that reaction 6 is not rate-limiting: the quasi-reversible waves we observe in cyclic voltammograms of $V(phen)_3^{2+}$, which we associate with the formation of $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$, are unaffected by saturation of the electrolyte solution with H_2O. (We estimate that the concentration of H_2O in the water-saturated CH_2Cl_2 solution is at least 0.1 M.[18]) Electrogenerated $V(NN)_3^{3+}$ is consumed much more quickly, however, in the presence of added pyridine or phenanthroline; thus, formation of $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ is controlled by the rate of reaction 7 under our conditions. Reaction 7 is itself likely to occur in several steps, involving a rapid deprotonation equilibrium to generate $V(phen)_2(H_2O)(OH)^{2+}$ followed by slow dimerization.[19] In this case the addition of excess base, increasing the concentration of species such as $V(phen)_2(H_2O)(OH)^{2+}$, would accelerate the overall reaction. These cyclic voltammetry measurements therefore complement the conclusions arrived at from our earlier photochemical studies.

Electrochemical Oxidation of $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$. Our experiments suggest that the following electrode processes occur in CH_3CN:

$$[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+} \rightarrow 2VO(phen)_2^{2+} + 2H^+ + 2e^- \quad (8)$$

$$VO(phen)_2^{2+} \rightleftarrows V(V) + e^- \quad (9)$$

$$VO(phen)_2^{2+} + e^- \rightleftarrows V(III) \quad (10)$$

Oxidation of $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ (corresponding to wave A in Figure 4) is irreversible; the most likely explanation is that rapid fragmentation occurs, generating $VO(phen)_2^{2+}$ (eq 8). The detailed mechanism of reaction 8 is not known, but it may involve initial one-electron oxidation of $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$, followed by cleavage to mononuclear vanadium(III) and vanadium(IV) complexes and subsequent rapid oxidation of the vanadium(III) complex. Reactions 9 and 10, which account for the remaining quasi-reversible waves in the voltammograms in Figure 4, are essentially those of mononuclear vanadium complexes.[11]

Our electrochemical measurements indicate that oxidation of $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ is more difficult than oxidation of mononuclear vanadium(III) (wave E in Figure 4; see eq 10). This is consistent with the observation that the binuclear form, $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$, is the more stable under our conditions. It is also in agreement with the mechanism proposed above for reaction 8: any mononuclear vanadium(III) species formed by one-electron oxidation of $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ and subsequent cleavage would be unstable with respect to further oxidation to vanadium(IV).

Chemical Oxidation of $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$. Our previous investigations[1] showed that photooxidation of $V(phen)_3^{2+}$

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(13) The electron-transfer product MV^+, which is ordinarily stable in aqueous solution, decomposes slowly (half-life ca. 10 h) in our experiments. This decomposition may be caused by traces of a redox-active impurity in the vanadium(III) starting material. Spontaneous reduction of MV^{2+} by $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ also occurs at pH 9.0 (borax buffer), but the MV^+ formed in these solutions disappears more quickly than at pH 8.0. For a discussion of the decomposition of MV^+, see: Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *13*, 155.

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(16) Bennett, L. E.; Taube, H. *Inorg. Chem.* **1968**, *7*, 254.

(17) The water exchange rate in $V(H_2O)_6^{3+}$, for example, is significantly greater than that in $V(H_2O)_6^{2+}$: Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenknopf, G. K. In *Coordinaton Chemistrty, Volume 2*; Martell, A. E., Ed.; ACS Monograph 174; American Chemical Society: Washington, DC, 1978, p 1.

(18) Linke, W. F. *Solubilities of Inorganic and Metal-Organic Compounds*; Van Nostrand: Princeton, NJ, 1958; p 1133.

(19) Spectroscopic evidence for the mononuclear complex "$V(phen)_2(OH)^{2+}$" (in aqueous solutions this species would be likely to exist as a six-coordinate adduct such as $V(phen)_2(H_2O)(OH)^{2+}$), in aqueous solutions at low vanadium concentrations, has recently been presented. Babenko, N. L.; Blokh, M. Sh. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1980**, *25*, 1481.

in unbufferd solutions results in net one-electron oxidation to $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$. Here we have shown that, in more basic solutions (pH ≥8), thermal electron transfer from $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ to various electron acceptors can also occur. This pH dependence is expected, on the basis of the vanadium(III)/vanadium(IV) electrode half-reaction:

$$[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+} \rightarrow 2VO^{2+} + 4phen + 2H^+ + 2e^- \quad (11)$$

Formation of VO^{2+} according to eq 11 should be favored at high pH (low $[H^+]$). Thus, photooxidation of $V(phen)_3^{2+}$ in unbuffered solution, which liberates H^+ (see reactions 6 and 7), is likely to produce a solution too acidic for further oxidation of vanadium(III).

Previous studies of the variation of electrode potentials with pH have treated vanadium ions in aqueous solutions[20] and, more recently, a variety of Ru and Os polypyridine complexes.[21] In the related complex $[(phen)_2Cr(\mu\text{-}OH)_2Cr(phen)_2]^{4+}$, deprotonation of the bridging hydroxy groups occurs in basic solutions;[22] such processes may also facilitate oxidation of $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$.

Our electronic absorption and ESR spectroscopic measurements show that at pH ≥8 $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ is readily oxidized to a vanadyl (VO^{2+}) species. This species may be $VO(phen)_2^{2+}$, although the stability of $VO(phen)_2^{2+}$ with respect to dissociation in aqueous solution is not well-known.[14,23,24]

We have also observed that the ESR signal due to the electron-transfer product, VO^{2+}, disappears slowly. We attribute this observation to the formation of a binuclear vanadium(IV) species:

$$2OH^- + 2VO^{2+} \rightleftarrows VO(\mu\text{-}OH)_2VO^{2+} \quad (12)$$

Unbuffered aqueous solutions separately prepared from $VO(phen)_2^{2+}$ are indefinitely stable. Solutions prepared in pH 8 buffer slowly lose their characteristic ESR signals, but the signals reappear immediately upon acidification of the solution.

Oxidation of $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ at pH 8, then, leads initially to a mononuclear VO^{2+} complex, but this material slowly hydrolyzes to form an ESR-silent binuclear species. Similar binuclear species, exhibiting strong antiferromagnetic coupling between the two vanadium atoms, have been proposed previously to explain the lack of ESR signals in basic vanadium(IV) solutions.[25] The $VO(\mu\text{-}OH)_2VO^{2+}$ structure has recently been confirmed in a crystallographic study by Wieghardt and co-workers;[26] their complex with 1,4,7-triazacyclononane also shows strong antiferromagnetism.

Photoinitiated Two-Electron Oxidation. Photooxidation of $V(phen)_3^{2+}$ results in the formation of $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$, which is stable in acidic solutions. However, in basic solutions the vanadium(III) dimer is capable of carrying out a second thermal electron transfer. Visible irradiation of a solution of $V(phen)_3^{2+}$ and MV^{2+} at pH 8 leads to rapid formation of MV^+ (identified by its electronic absorption spectrum) and VO^{2+} (identified by ESR). The overall sequence of reactions is summarized as follows:

$$V(phen)_3^{2+}(^4A_2) \xrightarrow{h\nu} V(phen)_3^{2+}(^4MLCT) \quad (13)$$

$$V(phen)_3^{2+}(^4MLCT) + A \rightarrow V(phen)_3^{3+} + A^- \quad (14)$$

$$2V(phen)_3^{3+} + 2H_2O \rightarrow [(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+} + 2phen + 2H^+ \quad (15)$$

$$[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+} + 2A \xrightarrow[\text{pH} \geq 8]{} 2VO^{2+} + 4phen + 2H^+ + 2A^- \quad (16)$$

Thus, photooxidation of $V(phen)_3^{2+}$ by one electron is followed by a spontaneous second electron transfer.[27] This represents the first example of photoinitiated two-electron transfer beginning with a d^3 metal complex. The strategy of sequential photochemical and thermal one-electron transfers has recently been employed by Nocera and Gray in the photooxidation of $Re_2Cl_8^{2-}$ to $Re_2Cl_9^-$.[28] However, our experiments differ from theirs in two respects. First, our two oxidations occur at a single metal center; this is probably facilitated by the formation of hydroxo and oxo complexes in the oxidized complexes.[29] Second, we have utilized the proton-transfer properties of the vanadium redox reactions to achieve one- and two-electron photochemistry by adjustment of pH.

We have demonstrated, therefore, that overall two-electron photooxidation can be accomplished in a mononuclear complex by finding conditions favorable for spontaneous oxidation of the initial photoredox product. We are currently exploring the capacity of other vanadium systems for two-electron transfer and the use of the final vanadyl products in efficient two-electron oxidation of substrate molecules in order to develop catalytic photochemical multielectron redox cycles.

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(27) Since $V(phen)_2(H_2O)(OH)^{2+}$,[19] formed by hydrolysis of $V(phen)_3^{3+}$, is also redox-active, it may also react spontaneously with MV^{2+}. This would lead to an alternative to eq 15 and 16, accomplishing the same net transformation without intermediate formation of $[(phen)_2V(\mu\text{-}OH)_2V(phen_2]^{4+}$:

$$V(phen)_3^{3+} + 2H_2O \rightarrow V(phen)_2(H_2O)(OH)^{2+} + phen + H^+$$

$$V(phen)_2(H_2O)(OH)^{2+} + A \rightarrow VO^{2+} + 2phen + H_3O^+ + A^-$$

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(29) Meyer and co-workers[21] have shown that the coupling of proton- and electron-transfer processes can make three or more consecutive oxidation states stable under very similar conditions. This "compression" of electrode potentials may be important in efficient catalysis of multielectron redox reactions.