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Synthesis and Reactivity of Oxo-Peroxo-Vanadium(V) Bipyridine Compounds

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The vanadium(IV) compound $[V^{IV}O(OH)(^{t}Bu_2bpy)_2]BF_4$ (**$V^{IV}O(OH)$**) ($^{t}Bu_2bpy$ = 4,4′-di-*tert*-butylbipyridine) is slowly oxidized by O_2 in ethereal solvents to give the oxo-peroxo compound $[V^{V}O(O_2)(^{t}Bu_2bpy)_2]BF_4$ (**$V^{V}O(O_2)$**) in excellent yield. This and related compounds were fully characterized by NMR, IR, and optical spectroscopies; mass spectrometry; elemental analyses; and an X-ray crystal structure of the 4,4′-dimethylbipyridine analog, $[V^{V}O(O_2)(Me_2bpy)_2]BF_4$. Monitoring the reaction of **$V^{IV}O(OH)$** with O_2 in THF/acetonitrile mixtures by ^{1}H NMR and optical spectroscopies surprisingly shows that the initial product is the *cis*-dioxo compound $[V^{V}(O)_2(^{t}Bu_2bpy)_2]BF_4$ (**$V^{V}O_2$**), which then converts to **$V^{V}O(O_2)$**. Reaction of **$V^{IV}O(OH)$** with $^{18}O_2$ gives ca. 60% triply ^{18}O labeled **$V^{V}O(O_2)$**. The mechanism of formation of **$V^{V}O(O_2)$** is complex and may occur via initial reduction of O_2 at vanadium(IV) to give a superoxo-vanadium(V) intermediate, autoxidation of the THF solvent, or both. That **$V^{V}O_2$** is generated first appears to be due to the ability of **$V^{IV}O(OH)$** to act as a hydrogen atom donor. For instance, **$V^{IV}O(OH)$** reacts with **$V^{V}O(O_2)$** to give **$V^{V}O_2$**. **$V^{V}O(O_2)$** is also slowly reduced to **$V^{IV}O(OH)$** by the organic hydrogen atom donors hydroquinone and TEMPOH (2,2,6,6-tetramethylpiperidin-1-ol) as well as by triphenylphosphine. Notably, the peroxo complex **$V^{V}O(O_2)$** is much less reactive with these substrates than the analogous dioxo compound **$V^{V}O_2$**.

Introduction

Oxo-peroxo-vanadium(V) compounds are of interest because of their presence in the haloperoxidase enzymes found in fungi and marine algae,[1] and their involvement in stoichiometric and catalytic oxidations of organic substrates.[2,3] These complexes are typically prepared by reacting vanadium(IV) or vanadium(V) complexes with hydrogen peroxide or alkylperoxides.[4] For catalytic applications, it is desirable to use O_2 as the oxidant, and there have been a few reports of the formation of oxo-peroxo-vanadium(V) products by reaction of O_2 with vanadium(IV) compounds.[5–8] These reactions are complicated by the mismatch in redox stoichiometry: oxidation of V^{IV} to V^{V} is a one-electron change, while reduction of dioxygen to peroxide is a two-electron process.

A particularly detailed study of a reaction of a vanadium(IV) complex with O_2, by Kelm and Krüger, showed using $^{18}O_2$-labeling that both peroxo oxygens in the oxo-peroxo-vanadium(V)-($py_2(NMe)_2$) product originated from dioxygen. A V^{V}-superoxo intermediate was also observed by EPR.[6] It was proposed that this species abstracts a hydrogen atom from the THF solvent followed by deprotonation of the resulting V^{V}-hydroperoxo species to give the final V^{V}-peroxo product. Similar mechanisms have been proposed by Kosugi et al. for autoxidation of their tris(3,5-diisopropylpyrazolyl)borate vanadyl complex,[5] and by Egdal et al. for their divanadium-phenoxyl-amine-pyridyl complexes.[8] Kotchevar et al. have also proposed reduction of O_2 by a vanadium(IV) (bis-cyclopentadienyl)(acetylacetonate) complex to give a vanadium(V) superoxo intermediate, which initiates peroxidation of lipids in liposomal membranes.[9] In contrast, Tajika et al. attribute formation of a $V^{V}O(O_2)$ product with a tris(2-pyridylmethyl)amine (TPA) ligand simply to peroxide formed in the solvent.[7] Autoxidation of solvent[10] to form catalytically active peroxo-vanadium species has also been

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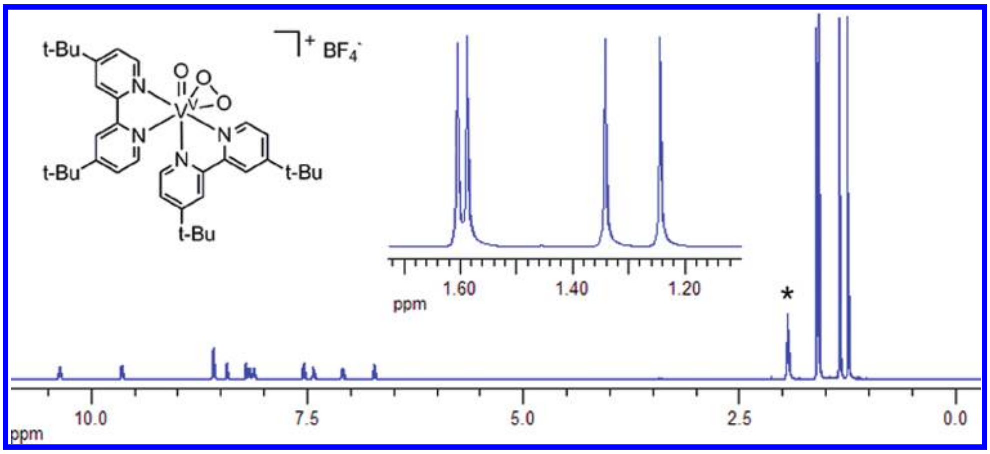


Figure 1. ^{1}H NMR of $\mathbf{V^VO(O_2)}$ in CD_3CN. The inset shows the ^{t}Bu region, and $*$ indicates the residual CD_2HCN solvent peak.

suggested in the catalytic epoxidation of olefins,[11] and alkane oxidation.[12]

Here, we report the oxidations of vanadium(IV)-oxo-hydroxo-bipyridine compounds by O_2 in THF to give oxo-peroxo-vanadium(V) products of the formula $[V^VO(O_2)(4,4'\text{-}R_2bpy)_2]BF_4$ (R = ^{t}Bu, Me, H). Bipyridine is a classic ligand for vanadium(IV) and vanadium(V), but the prior literature in this area has some inconsistencies, as described below. We came across these issues as part of our studies of hydrogen atom transfer reactions interconverting dioxo-vanadium(VI) and oxo-hydroxo-vanadium(IV) complexes.[13] This report discusses the nature of the O_2 reactions and their mechanisms and describes reactions of the peroxo complex $[V^VO(O_2)(4,4'\text{-}^tBu_2bpy)_2]BF_4$ with triphenylphosphine and hydrogen atom donors. This system is unusual because the vanadium(IV) compound itself can act as a hydrogen atom donor and because the peroxovanadium(V) complex is remarkably stable.

Results

A. Synthesis and Characterization of $[V^VO(O_2)(4,4'\text{-}^tBu_2bpy)_2]BF_4$, $[V^VO(O_2)]$. In an attempt to synthesize the dioxo-vanadium(V) compound $[V^V(O)_2(^tBu_2bpy)_2]BF_4$ $[\mathbf{V^VO_2}]$,[13] the known vanadium(IV) hydroxo complex $[V^{IV}O(OH)(^tBu_2bpy)_2]BF_4$ $[\mathbf{V^{IV}O(OH)}]$[14] was stirred in THF while exposed to air. This followed a very similar procedure described by Brand et al. for the aerobic oxidation of the related vanadyl-chloride complex with unsubstituted bipyridine ligands, $[V^{IV}O(Cl)(bpy)_2]ClO_4$.[15] In this study, we have mostly used the 4,4′-^{t}Bu$_2$bpy ligand because it gives complexes with higher solubility in organic solvents, and because the vanadium(IV) derivative $\mathbf{V^{IV}O(OH)}$ has an easily observed, characteristic ^{1}H NMR spectrum with four separate ^{t}Bu resonances.[13] Over three days at ambient temperatures under air, a yellow suspension of the partially soluble $\mathbf{V^{IV}O(OH)}$ in THF transforms into a red suspension, and addition of pentane yields a pale red solid in 97% yield. As described below, NMR, UV−vis, IR, and ESI-MS methods indicate this product is not the anticipated dioxo-vanadium(V) complex but is instead an oxo-peroxo-vanadium(V) species, $[V^VO(O_2)(^tBu_2bpy)_2]BF_4$ $[\mathbf{V^VO(O_2)}]$ (eq 1). The peroxo complex is formed in high yield using either 1 atm of air or 1 atm of dry O_2, but no reaction is observed under an atmosphere of N_2. The reaction proceeds well in dry THF distilled from Na/Ph$_2$CO, or in unpurified (wet) THF from a bottle on the benchtop, which contains 250 ppm of the stabilizer BHT (butylated hydroxytoluene, 2,6-^{t}Bu$_2$-4-Me-C_6H_2OH). Et$_2$O or CH$_3$CN/THF mixtures can also be used as the solvent, but no reaction is observed when $\mathbf{V^{IV}O(OH)}$ is exposed to an atmosphere of O_2 in CD_3CN or CD_2Cl_2 for three weeks. Thus, $\mathbf{V^{IV}O(OH)}$ has been observed to convert to $\mathbf{V^VO(O_2)}$ only when both O_2 and an ethereal solvent are present (although perhaps materials with weak C−H bonds other than ethers could also be effective).

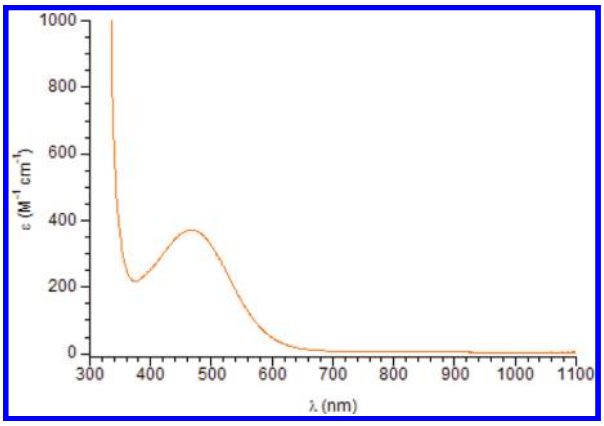
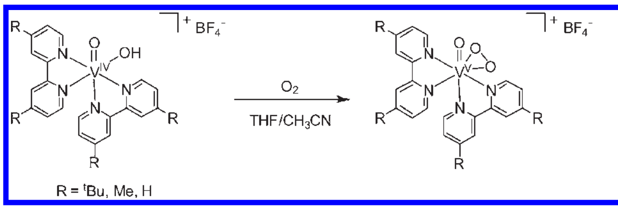


Figure 2. UV−vis spectrum of $\mathbf{V^VO(O_2)}$ in acetonitrile.



(1)

^{1}H NMR spectra of $\mathbf{V^VO(O_2)}$ show that the compound is diamagnetic. The presence of 4 ^{t}Bu and 12 bpy peaks

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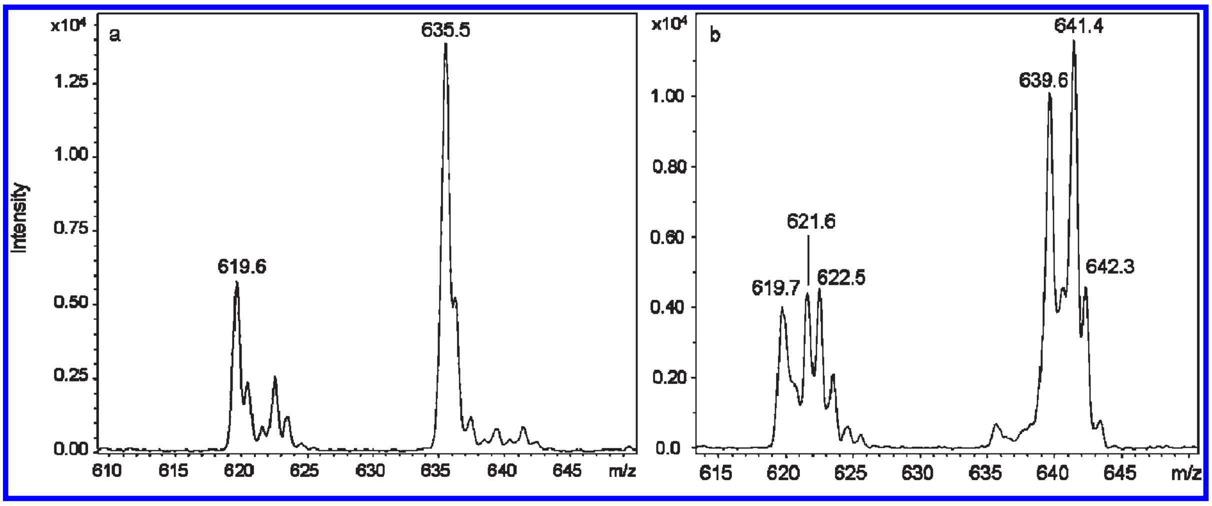

Figure 3. ESI-MS spectra of reaction mixtures of (a) V^{IV}O(OH) with ^{16}O$_2$ in THF and (b) V^{IV}O(OH) with ^{18}O$_2$ in THF.

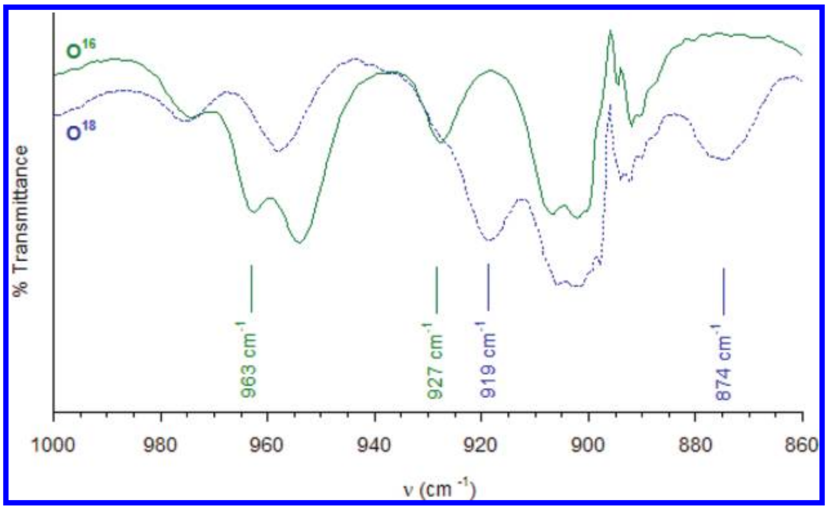

Figure 4. IR spectra of solutions of **V$^{\mathbf{V}}$O(O$_2$)** (solid green line) and **V$^{\mathbf{18}}$O($^{\mathbf{18}}$O$_2$)** (dashed blue line) in dichloromethane.

indicates a C_1 symmetric complex containing two inequivalent 4,4′-^{t}Bu$_2$bpy ligands (Figure 1). Assignments of the ^{1}H NMR spectrum were enabled by a combination of ^{1}H 2D COSY and 2D NOESY NMR spectra. The UV−vis spectrum of **V$^{\mathbf{V}}$O(O$_2$)** in CH$_3$CN shows a peak at 475 nm with an ε of 370 M^{-1} cm^{-1} (Figure 2), typical for a peroxo-to-vanadium charge-transfer transition.[16] More intense peaks are also observed below 350 nm, presumably due to bipyridine $\pi \rightarrow \pi^*$ absorptions since similar bands appear in spectra of **V$^{\mathbf{IV}}$O(OH)**.

ESI-MS analysis of an acetonitrile solution of **VO(O$_2$)** from O$_2$ shows a base peak at 635.5 m/z, the predicted mass for the [V^{V}O(O$_2$)(^{t}Bu$_2$bpy)$_2$]$^+$ cation (Figure 3a). Isolation of the 635.5 peak followed by collision induced fragmentation yields one intense peak at 367.1 Da, corresponding to the loss of one ^{t}Bu$_2$bpy ligand to give a [VO(O$_2$)^{t}Bu$_2$bpy]$^+$ fragment. FAB/MS using a nitrobenzyl alcohol matrix shows analogous results. The peak with an m/z of 619.6 in Figure 3a corresponds to a **V$^{\mathbf{V}}$O$_2$** impurity in this sample.

A suspension of **V$^{\mathbf{IV}}$O(OH)** in THF was stirred under ca. 1 atm of ^{18}O$_2$ (98.4% enriched), to probe how many O atoms from O$_2$ are incorporated in the product. ESI-MS spectra of the resulting ^{18}O-labeled product have their most intense peak at m/z = 641.4 (Figure 3b). This is 6 Da larger than the most intense peak observed for **V$^{\mathbf{16}}$O($^{\mathbf{16}}$O$_2$)**, indicating incorporation of three ^{18}O atoms. Isolation and fragmentation of the 641 m/z peak yields a peak at 372.8 m/z, consistent with [V^{18}O(^{18}O$_2$)^{t}Bu$_2$bpy]$^+$ and further supporting the presence of three ^{18}O atoms. There is a less intense peak at 639.6 m/z, corresponding to doubly ^{18}O labeled **V$^{\mathbf{V}}$O(O$_2$)**, but no peaks are observed at m/z = 635 or 637. Thus, all of the **V$^{\mathbf{V}}$O(O$_2$)** generated is at least doubly ^{18}O labeled, and ~60% is triply labeled on the basis of the peak heights. Residual **V$^{\mathbf{V}}$O$_2$** and **V$^{\mathbf{IV}}$O(OH)** present in the reaction mixture give rise to peaks at 619.7, 621.6, and 622.5 m/z, indicating the presence of unlabeled and singly- and doubly-^{18}O labeled materials.

V$^{\mathbf{V}}$O(O$_2$) was also characterized by IR spectroscopy. Oxo-peroxo-vanadium complexes are known to have strong, distinct V═O and O−O IR stretches,[3] and assignments of these stretches for **V$^{\mathbf{V}}$O(O$_2$)** were confirmed by ^{18}O labeling studies. The isotopic shifts are most clear in spectra obtained from dichloromethane solutions, as shown in Figure 4. The ^{16}O compound shows a ν(V═^{16}O) stretch at 963 cm^{-1} and a ν(^{16}O−^{16}O) stretch

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at 927 cm^{-1}, typical values for oxo-peroxo-vanadium compounds.[3,17] In the complex prepared from $^{18}O_2$, which is predominantly triply ^{18}O enriched, new peaks for $\nu(V{=}^{18}O)$ and $\nu(^{18}O{-}^{18}O)$ appear at 919 and 874 cm^{-1}, respectively. These isotopic shifts agree well with those predicted from a simple diatomic oscillator model, 917 and 874 cm^{-1}. The formation of triply labeled $\mathbf{V^VO(O_2)}$ was unexpected, but exchange of ^{18}O labels between peroxide, water, and terminal oxo groups has been previously reported for oxo-peroxo-vanadium compounds.[6,18]

The analogs of $\mathbf{V^{IV}O(OH)}$ with 4,4′-dimethyl-bipyridine and bipyridine ligands $[V^{IV}O(OH)(Me_2bpy)_2]BF_4$ and $[V^{IV}O(OH)(bpy)_2]BF_4$ show very similar chemistry.[13] These complexes are insoluble in pure THF, so their reactions with O_2 were performed in 1:1 CH_3CN/THF mixtures. Over 24 h under air, these solutions changed from yellow to orange, and $[V^VO(O_2)(Me_2bpy)_2]BF_4$ and $[V^VO(O_2)(bpy)_2]BF_4$ were obtained in moderate yields after removal of solvent and washing with *n*-pentane. The NMR and UV−vis spectra of the latter complex match those of the reported perchlorate salt, $[V^VO(O_2)(bpy)_2]ClO_4$, which was prepared following the more typical method of addition of H_2O_2 to an acidic mixture of V_2O_5 and ligand.[19] For both $[V^VO(O_2)(Me_2bpy)_2]BF_4$ and $[V^VO(O_2)(bpy)_2]BF_4$, ^1H NMR spectra in CD_3CN or CD_2Cl_2 indicate diamagnetic, C_1-symmetric cations with two bipyridine ligands, similar to $\mathbf{V^VO(O_2)}$. ESI-MS and FAB-MS show peaks consistent with $[V^VO(O_2)(Me_2bpy)_2]^+$ and $[V^VO(O_2)(bpy)_2]^+$, and the IR spectra of these compounds are similar to the spectrum of $\mathbf{V^VO(O_2)}$ as well. $[V^VO(O_2)(Me_2bpy)_2]BF_4$, for instance, shows a $\nu(V{=}O)$ stretch at 946 cm^{-1} and a $\nu(O{-}O)$ stretch at 923 cm^{-1}.

X-ray quality crystals of $[V^VO(O_2)(Me_2bpy)_2]BF_4$ were obtained by slow diffusion of Et_2O into a concentrated CH_3CN solution of $[V^VO(O_2)(Me_2bpy)_2]BF_4$ in an NMR tube. The resulting structure suffers from whole molecule disorder, whereby a noncrystallographic 2-fold axis through the vanadium center rotates the oxo group into the peroxo group.[20a] Because of this disorder, all non-hydrogen atoms, except for V1, were refined isotropically, but no restraints were used. The BF_4^- anion is also rotationally disordered and was treated using the SQUEEZE routine.[20b] Half of the disordered cation is shown in Figure 5. Crystallographic information is given in Table 1, and selected bond lengths and angles for half of the disordered cation (which are within error of the values for the other half) are given in Table 2.

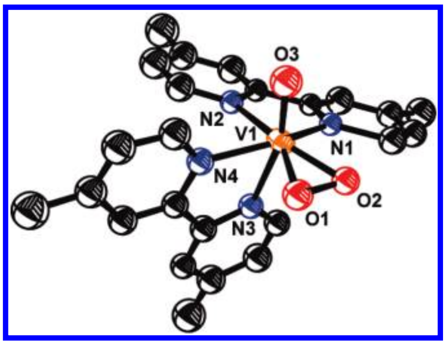

Figure 5. ORTEP of the cation in $[V^VO(O_2)(Me_2bpy)_2]BF_4$, with hydrogen atoms omitted for clarity.

Table 1. X-Ray Crystallographic Data for $[V^VO(O_2)(Me_2bpy)_2]BF_4$

empirical formula	$C_{24}H_{24}BF_4N_4O_3V$
fw	554.22
cryst syst	monoclinic
space group	*P*2(1)/*c*
a (Å)	14.190(5)
b (Å)	16.245(6)
c (Å)	10.876(4)
α (deg)	90
β (deg)	98.568(4)
γ (deg)	90
volume (Å^3)	2479.1(16)
Z	4
density (g/cm^3, calcd)	1.485
μ (mm^{-1})	0.465
λ (Å)	0.71073
cryst size (mm)	0.15 × 0.12 × 0.10
temperature (K)	130(2)
θ range (deg)	2.51−25.57
index ranges	$-17 \le h \le 17$
	$-19 \le k \le 16$
	$-12 \le l \le 13$
refls collected	22202
data/restraints/params	4548/0/261
R_{int}	0.0429
R_1, wR_2 (I > 2σI)	0.0771, 0.2357
goodness of fit	1.061

Table 2. Selected Bond Lengths and Angles for $[V^VO(O_2)(Me_2bpy)_2]BF_4$

bond length (Å)		angle (deg)	
V1−O1	1.869(7)	O3−V1−O1	104.4(3)
V1−O2	1.877(7)	O3−V1−O2	105.0(3)
V1−O3	1.556(7)	O1−V1−O2	44.0(3)
O1−O2	1.402(10)	N1−V1−N2	67.2(4)
V1−N1	2.198(12)	N3−V1−N4	73.6(4)
V1−N2	2.334(11)		
V1−N3	2.263(9)		
V1−N4	2.205(10)		

The X-ray structure of $[V^VO(O_2)(Me_2bpy)_2]BF_4$ is consistent with all of the spectroscopic results discussed above and is similar to reported oxoperoxo-vanadium(V) structures.[3] The O−O bond length of 1.402(10) Å is ~0.02−0.07 Å shorter than in most other oxoperoxo-vanadium(V) structures,[3] however. This shorter than expected bond length may be due to the disorder between the oxo and peroxo moieties in the structure. Notably, the O−O bond length observed here is more reasonable than the previously reported, very short distances of 1.24 and 1.3 Å for $[V^VO(O_2)(bpy)_2]ClO_4$ and $[V^VO(O_2)(phen)_2]ClO_4$ (phen = 1,10 phenanthroline), respectively.[19] The unusually short O−O distances in the previously reported structures are likely due to unrecognized disorder between the oxo and peroxo moieties, similar to what is observed here in $[V^VO(O_2)(Me_2bpy)_2]BF_4$. Additionally, the V═O bond length of 1.556(7) Å in $[V^VO(O_2)(Me_2bpy)_2]BF_4$ is ~0.04−0.06 Å shorter than is typical

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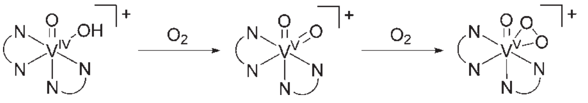
in oxoperoxo-vanadium(V) structures, which may also reflect the disorder. The strong trans effect of the oxo and peroxo groups causes a significant lengthening of the V−N bonds trans to these groups.

B. Mechanistic Experiments. To probe the mechanism of formation of $\mathbf{V^{V}O(O_{2})}$, the reaction of $\mathbf{V^{IV}O(OH)}$ with O_2 in CH_3CN/THF solution was monitored by optical spectroscopy (Figure 6a and c). The THF was distilled from Na/benzophenone ketyl, so that no organic peroxides or peroxide inhibitors were present initially. After an induction period of ca. 1 h, the $\mathbf{V^{IV}O(OH)}$ (λ_{max} = 400 nm) began to bleach *without* concomitant formation of any $\mathbf{V^{V}O(O_{2})}$ for the next 5 h, on the basis of the absence of its characteristic optical band at 475 nm. The bleaching indicates formation of $\mathbf{V^{V}O_{2}}$, as shown by the ^{1}H NMR experiments below. Only after ≥80% of the $\mathbf{V^{IV}O(OH)}$ disappeared did $\mathbf{V^{V}O(O_{2})}$ form in observable amounts, and this peroxo product continued to form over the next 25 h to give the final 98% yield. ^{1}H NMR spectra of the resulting solution showed only $\mathbf{V^{V}O(O_{2})}$, and what appeared to be THF oxidation products. GC-MS of the organic products after reaction showed formation of the γ-butyrolactone and 2-hydroxy-THF, consistent with the peaks observed by ^{1}H NMR. A similar reaction, with $\mathbf{V^{IV}O(OH)}$ under an atmosphere of O_2 in a cuvette but wrapped in aluminum foil and stored in the dark, gave a quantitative yield of $\mathbf{V^{V}O(O_{2})}$ by optical spectroscopy when checked after 2 days. The induction period observed in these reactions varied considerably, ranging from hours to several days. The reaction of a 1:1 mixture of $\mathbf{V^{IV}O(OH)}$ and $\mathbf{V^{V}O_{2}}$ (each 3 mM) in CH_3CN/THF with O_2 was also monitored by optical spectroscopy. After an induction period of several days, the $\mathbf{V^{IV}O(OH)}$ bleached, indicating its conversion to $\mathbf{V^{V}O_{2}}$. All the $\mathbf{V^{V}O_{2}}$ present was then converted to $\mathbf{V^{V}O(O_{2})}$ in just one day. The cis-dioxo compound $\mathbf{V^{V}O_{2}}$ therefore appears to be a kinetically competent intermediate for this reaction.

The reaction of $\mathbf{V^{IV}O(OH)}$ with O_2 was also monitored by ^{1}H NMR in THF-d_8/CD_3CN. By NMR, the broad, paramagnetic ^{t}Bu peaks of $\mathbf{V^{IV}O(OH)}$[13] disappear over two days, forming predominantly the known *cis*-dioxo vanadium(V) complex $[V^{V}(O)_2(^{t}Bu_2bpy)_2]BF_4$,[13] with small (ca. 1%) amounts of $\mathbf{V^{V}O(O_{2})}$ (eq 2). $\mathbf{V^{V}O_{2}}$ then slowly disappears, quantitatively forming $\mathbf{V^{V}O(O_{2})}$. This is consistent with the optical experiments above: $\mathbf{V^{IV}O(OH)}$ first bleaches to form $\mathbf{V^{V}O_{2}}$, which is d^0 and has no characteristic optical absorbance; then $\mathbf{V^{V}O_{2}}$ is converted to $\mathbf{V^{V}O(O_{2})}$.



(2)

To test for possible binding of O_2 to the vanadium(IV) complex $\mathbf{V^{IV}O(OH)}$, optical spectra were taken of a CH_3CN/THF solution of $\mathbf{V^{IV}O(OH)}$ before and immediately after O_2 was added. There is no perceptible difference between these spectra, indicating no significant formation of a dioxygen adduct under these conditions.

The experiments above implicate $\mathbf{V^{V}O_{2}}$ as an important intermediate in the reaction of $\mathbf{V^{IV}O(OH)}$ with O_2. Therefore, its reactivity with O_2 has also been examined. Remarkably, solutions of $\mathbf{V^{V}O_{2}}$ in CH_3CN/THF react with air to quantitatively form the peroxo complex $\mathbf{V^{V}O(O_{2})}$ (eq 3). This reaction is significantly slower than the one starting from $\mathbf{V^{IV}O(OH)}$, requiring a week to proceed to completion (Figure 6b and c). An ^{1}H NMR spectrum of an aliquot of this solution in CD_3CN after complete reaction shows only $\mathbf{V^{V}O(O_{2})}$, THF, and THF oxidation products. $\mathbf{V^{V}O_{2}}$ is more rapidly converted to $\mathbf{V^{V}O(O_{2})}$ in the presence of ca. 5 equiv of the alkylperoxide ^{t}BuOOH in CD_3CN, by NMR.

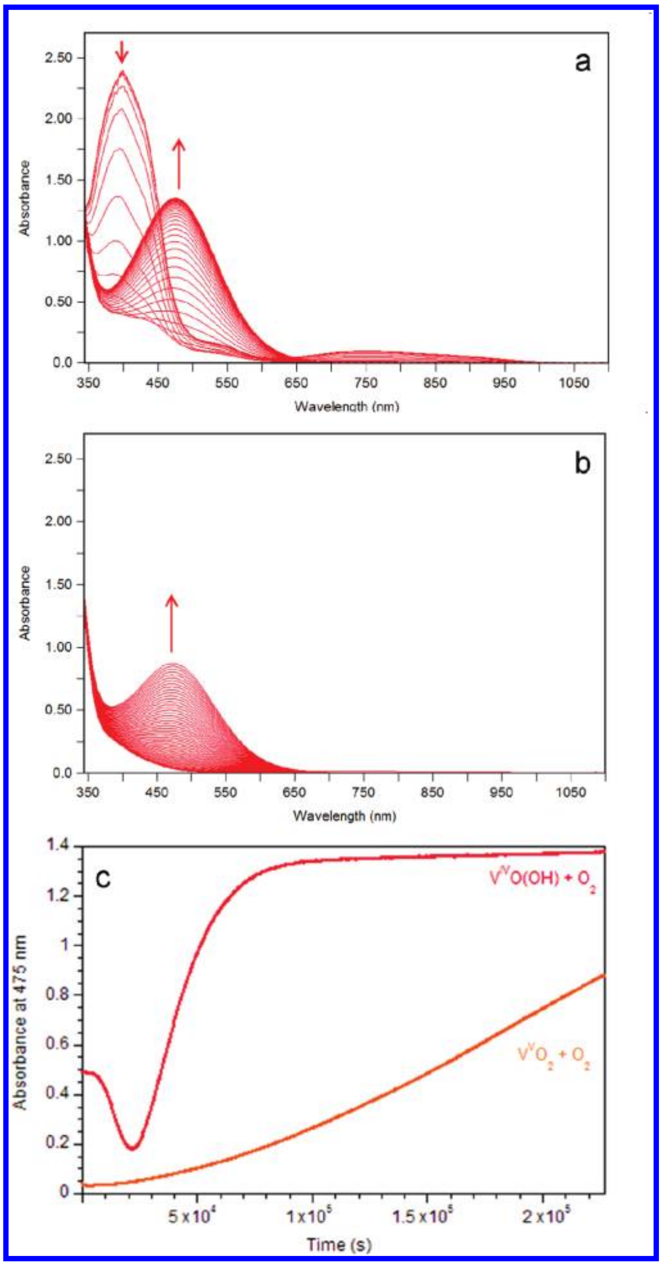
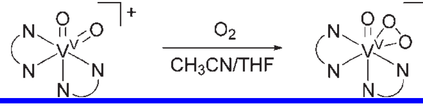
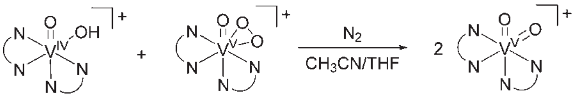


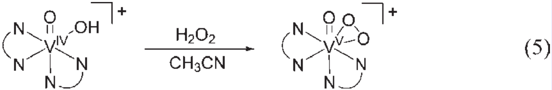
Figure 6. UV−vis spectra of reaction of (a) $V^{IV}O(OH)$ with O_2 in THF/CH_3CN, (b) $V^{V}O_2$ with O_2 in THF/CH_3CN, and (c) a comparison of absorbance at 475 nm versus time.



(3)

We have also found that isolated $\mathbf{V^{IV}O(OH)}$ quantitatively reacts with $\mathbf{V^{V}O(O_{2})}$ in THF/MeCN to give $\mathbf{V^{V}O_{2}}$ over several hours (eq 4). In this comproportionation reaction, the vanadium center of **V^{IV}O(OH)** is oxidized to vanadium(V) while the peroxo ligand of **V^{V}O(O$_2$)** is reduced to an oxo group. This reaction was monitored by UV−vis spectroscopy, and the final vanadium products were confirmed by ^{1}H NMR. Interestingly, only 1 equiv of **V^{IV}O(OH)** is consumed in the reduction of 1 equiv of **V^{V}O(O$_2$)**. In the opposite direction, **V^{IV}O(OH)** in CD_3CN reacts with ~1 equiv of 30% aqueous H_2O_2 over 3 h at room temperature to give **V^{V}O(O$_2$)** in good yield (by ^{1}H NMR, eq 5).

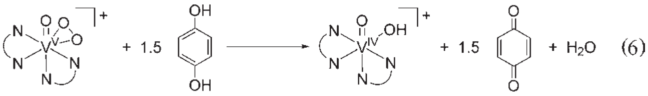

(4)


(5)

C. Reactivity of the Peroxo Complex [V^{V}O(O$_2$)(*^{t}*Bu$_2$bpy)$_2$]BF$_4$ [V^{V}O(O$_2$)]. Solid **V^{V}O(O$_2$)** is very stable, lasting years on the benchtop, and solutions in CD_3CN over many days show no decomposition. **V^{V}O(O$_2$)** reacts with Ph_3P (1.5 equiv) over a week in dry CD_3CN in a J. Young NMR tube, with the orange solution turning yellow. By both ^{1}H and ^{31}P NMR spectroscopies, the PPh_3 is converted to Ph_3PO, with only Ph_3PO visible in ^{31}P NMR spectra after one week. In the ^{1}H NMR spectra, broad peaks corresponding to the ^{t}Bu groups of **V^{IV}O(OH)** grow as **V^{V}O(O$_2$)** is reduced. A small amount of free ligand (ca. 10%) is also generated during the reaction, indicating that some other minor vanadium products must be formed. With 4.4 equiv of Ph_3P, the reaction reaches completion in approximately 3.5 days, and ca. 1.7 equiv of Ph_3P are oxidized to Ph_3PO.

No **V^{V}O$_2$** is observed in the NMR spectra of the reaction of **V^{V}O(O$_2$)** with PPh_3. This is surprising as most d^0 peroxo complexes are reduced by phosphines to give the corresponding d^0 oxo compounds.[21] In this case, however, separate control experiments show that **V^{V}O$_2$** reacts with Ph_3P faster than the peroxo complex, with the reactions reaching completion within 4 h. This reaction gives 0.5 equiv of Ph_3PO, approximately 0.5 equiv of **V^{IV}O(OH)**, free ligand, and other unknown products with broad peaks in the ^{t}Bu region, by ^{1}H NMR. Peroxovanadium(V) complexes are also known to transfer an oxygen atom to olefins to give epoxides,[2] but no reaction was observed between **V^{V}O(O$_2$)** and *trans*-stilbene in acetonitrile over one week at 25 °C.

V^{V}O(O$_2$) also reacts with hydrogen atom donors. The presence of 6 equiv of hydroquinone reduces **V^{V}O(O$_2$)** to **V^{IV}O(OH)** in 90% yield (some free ligand is generated) in dry CD_3CN over 5 days, as monitored by ^{1}H NMR. The reaction reaches completion overnight at 50 °C with 10 equiv of hydroquinone. A total of 1.5 equiv of hydroquinone are consumed per vanadium, and an equal amount of benzoquinone grows in over the course of the reaction, as does H_2O. Equation 6 shows the balanced reaction, with three reducing equivalents of hydroquinone consumed to reduce the peroxo ligand by 2e$^-$ and the vanadium center by 1e$^-$.


(6)

V^{V}O(O$_2$) is also reduced by 2 equiv of the hydroxylamine 2,2,6,6-tetramethyl-*N*-hydroxypiperidine (TEMPOH). Over 24 h, all of the TEMPOH is consumed while approximately 60% of **V^{V}O(O$_2$)** is reduced to **V^{IV}O(OH)**. Three equivalents of TEMPOH would be required to fully reduce **V^{V}O(O$_2$)** to **V^{IV}O(OH)**, but substoichiometric amounts of TEMPOH were used to avoid the competitive reaction of TEMPOH with **V^{IV}O(OH)**.[13]

Discussion

A. Synthesis of the Peroxo Complex V^{V}O(O$_2$). The formation of a vanadium(V) peroxo complex from a vanadium(IV) species and O_2 is a surprising reaction because of the mismatch in redox stoichiometry. The vanadium is oxidized by one electron, and the dioxygen is reduced by 2e$^-$. It is even more odd that **V^{V}O(O$_2$)** is formed quantitatively from the vanadium(V) dioxo complex **V^{V}O$_2$** and O_2 in CH_3CN/THF, without any redox change at the vanadium. In these reactions, the ether solvent provides some or all of the reducing equivalents needed to form the peroxo ligand, as indicated by the formation of γ-butyrolactone and 2-hydroxy-THF from THF. In the absence of a reducing solvent, in CH_2Cl_2 or MeCN, **V^{IV}O(OH)** is unreactive with O_2. The formation of oxidized THF products upon reaction of a vanadium(IV) complex with O_2 has previously been reported,[6] as have stoichiometric and catalytic aerobic oxidations of THF mediated by a variety of transition metal and main group complexes.[22]

We originally investigated the reaction of **V^{IV}O(OH)** with O_2 on the basis of the report of Brand et al. that [V^{IV}(O)Cl(bpy)$_2$]Cl in THF is oxidized by O_2 to [V^{V}(O)$_2$(bpy)$_2$]Cl. Their product was characterized by elemental analysis, IR, and optical spectroscopies and an X-ray crystal structure.[15] Brand et al.'s report contrasts with our observations that the related hydroxy complexes [V^{IV}(O)OH(R$_2$bpy)$_2$]BF$_4$ react with O_2 to yield oxo-peroxo complexes and form dioxo species only as transient intermediates. In retrospect, it appears that the product prepared by Brand et al. most likely contained a substantial amount of the peroxo complex. Most notably, the optical spectrum of Brand et al.'s "[V^{V}(O)$_2$(bpy)$_2$]Cl" is reported to have a peak at 475 nm with a molar absorptivity of 340 M^{-1} cm^{-1}, a transition characteristic of oxoperoxovanadium(V) compounds.[3]

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(22) cf., (a) Morales-Juarez, J.; Cea-Olivares, R.; Moya-Cabrera, M. M.; Jancik, V.; Garcia-Montalvo, V.; Toscano, R. A. *Inorg. Chem.* **2005**, *44*, 6924–6926. (b) Moreira, R. F.; Tshuva, E. Y.; Lippard, S. J. *Inorg. Chem.* **2004**, *43*, 4427–4434. (c) Zhang, C. X.; Liang, H.; Kim, E.; Shearer, J.; Helton, M. E.; Kim, E.; Kaderli, S.; Incarvito, C. D.; Zuberbuhler, A. D.; Rheingold, A. L.; Karlin, K. D. *J. Am. Chem. Soc.* **2003**, *125*, 634–635. (d) Straub, T.; Koskinen, A. M. P. *Inorg. Chem. Commun.* **2002**, *5*, 1052–1055. (e) Reetz, M. T.; Toller, K. *Tetrahedron Lett.* **1995**, *36*, 9461–9464. (f) Sommovigo, M.; Alper, H. *J. Mol. Catal.* **1981**, 151–158. (g) MacDonnell, F. M.; Fackler, N. L. P.; Stern, C.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1994**, *116*, 7431–7432. (h) Li, P.; Alper, H. *J. Mol. Catal.* **1992**, 143–152. (i) Hirai, K.; Nutton, A.; Maitlis, P. M. *J. Mol. Catal.* **1981**, *10*, 203–211.

The $[V^VO(O_2)(bpy)_2]BF_4$ reported here has this band at $\lambda = 475$ nm and $\varepsilon = 370$ M^{-1} cm^{-1}. In contrast, the authentic *cis*-dioxo compound, $[V^V(O)_2(bpy)_2]BF_4$, is yellow with no distinct peaks above 350 nm.[13] Our assignments have been confirmed by ^1H NMR spectra, which Brand et al. did not report. They do give an elemental analysis of the chloride hydrate, "$[V^V(O)_2(bpy)_2]Cl\cdot H_2O$", but this has a calculated elemental composition that is essentially indistinguishable from the peroxo compound $[V^VO(O_2)(bpy)_2]Cl$. The dioxo cation $[V^V(O)_2(bpy)_2]^+$ has now been reported four times, with Brand et al.'s report being the first, the next two being hydrothermal syntheses where only single crystals were characterized.[23] In light of these issues, we recommend synthesizing the simple $[V^V(O)_2(R_2bpy)_2]^+$ salts directly from aqueous vanadate and the bipyridine ligand, as we recently reported.[13]

B. Comments on the Mechanism of Formation of the Peroxo Complex $\mathbf{V^VO(O_2)}$. The mechanism of conversion of $\mathbf{V^{IV}O(OH)}$ to $\mathbf{V^VO(O_2)}$ is clearly complex. As mentioned above, two types of mechanisms have been discussed for the oxidation of vanadium(IV) compounds by O_2. Initial binding of O_2 to a vanadium(IV) species could form a vanadium(V)-superoxide complex. Such a V^V-$(O_2^{\bullet-})$ species has been prepared electrochemically and observed by ESR by Kelm and Krüger, although it was generated by oxidation of a V^V-peroxo complex rather than from $V^{IV} + O_2$.[6] If the chemistry described here proceeds via initial binding of O_2 to V^{IV}, this must be an unfavorable equilibrium since no spectral change is observed when O_2 is added to solutions of $\mathbf{V^{IV}O(OH)}$ and no reaction is observed in the absence of an ether solvent. One could imagine a pathway in which an unobserved vanadium(V)-oxo-superoxo intermediate such as "$[(^tBu_2bpy)_2V^VO(O_2^{\bullet-})]^{2+}$" abstracts a hydrogen atom from $\mathbf{V^{IV}O(OH)}$, yielding $\mathbf{V^VO_2}$ and $\mathbf{V^VO(O_2)}$ and H^+.[5] The $\mathbf{V^VO(O_2)}$ would then be reduced by another equivalent of $\mathbf{V^{IV}O(OH)}$ to form more $\mathbf{V^VO_2}$. This reduction of $\mathbf{V^VO(O_2)}$ is likely to occur via formation of vanadium-hydroperoxo intermediates, which may generate small amounts of reactive organic species via homolysis of a VO−OH bond[24] or oxidation of THF. However, such a pathway does not explain the induction period or lack of autoxidation of $\mathbf{V^{IV}O(OH)}$ in less oxidizable solvents.

It has also been suggested that organic peroxides play a key role in the aerobic formation of vanadium peroxides from vanadium(IV) starting materials.[7,11,12] The above observations and the presence of a variable induction period for the bleaching of $\mathbf{V^{IV}O(OH)}$ is consistent with such a pathway, where unobserved reactive intermediates require some time to reach sufficient concentrations. The reaction does not appear to be initiated by reactive species already present in the solvent, such as an organic hydroperoxide, as it proceeds similarly in "benchtop" THF and THF freshly distilled from benzophenone ketyl. It is not evident what process generates the reactive intermediates, as $\mathbf{V^{IV}O(OH)}$ is quite stable in THF and THF/CH_3CN mixtures in the absence of O_2. The observation of oxidized THF products is consistent with both this mechanism and the one in the previous paragraph.

The initially observed product of air oxidation of $\mathbf{V^{IV}O(OH)}$ is $\mathbf{V^VO_2}$ (eq 2, Figure 6a), but this is not mechanistically very informative. $\mathbf{V^VO_2}$ could form directly, but it is also possible that the initial product is $\mathbf{V^VO(O_2)}$, which rapidly comproportionates with $\mathbf{V^{IV}O(OH)}$ to give $\mathbf{V^VO_2}$ (eq 4). This is a unique feature of this system, probably related to the ability of $\mathbf{V^{IV}O(OH)}$ to act as a hydrogen atom donor. In previous work,[13] $\mathbf{V^{IV}O(OH)}$ was shown to have a weak O−H bond, with a bond dissociation free energy (BDFE)[25] of only 70.6 kcal mol^{-1}. For instance, $\mathbf{V^{IV}O(OH)}$ reversibly transfers a hydrogen atom to the stable phenoxyl radical 2,6-di-*tert*-butyl-4-methoxy-phenyl ($ArO^\bullet$), forming an equilibrium with $\mathbf{V^VO_2}$ and the corresponding phenol. Thus, the reduction of $\mathbf{V^VO(O_2)}$ by $\mathbf{V^{IV}O(OH)}$ is very similar to the reductions of $\mathbf{V^VO(O_2)}$ by the organic H-atom transfer agents TEMPOH and hydroquinone.

The conversion of $\mathbf{V^VO_2}$ to $\mathbf{V^VO(O_2)}$ with O_2, with its unusual stoichiometry of $2e^-$ reduction of O_2 without a change in the vanadium oxidation state (eq 3, Figure 5b), must also have a complex mechanism. Again, the data are consistent with the reaction being mediated by small concentrations of reactive oxygen species. In particular, $\mathbf{V^VO_2}$ is consumed faster when it is formed as an intermediate in reactions of $\mathbf{V^{IV}O(OH)}$, in which reactive species have presumably built up to significant concentrations. The observation that ^tBuOOH converts $\mathbf{V^VO_2}$ to $\mathbf{V^VO(O_2)}$ implies that this transformation could be accomplished by other hydroperoxides, such as the autoxidation intermediate 2-hydroperoxy-THF.[26] Additionally, $\mathbf{V^VO_2}$ may be capable of abstracting $H^\bullet$ from the THF solvent to start an autoxidation radical chain, as $\mathbf{V^VO_2}$ is known to stoichiometrically abstract $H^\bullet$ from xanthene and dihydroanthracene under anaerobic conditions. These species, however, have very weak C−H bonds (bond dissociation enthalpies ~ 80 kcal mol^{-1}), close to that of $\mathbf{V^{IV}O(OH)}$ and substantially weaker than the α-C−H bonds of THF (BDE 92 kcal mol^{-1}).[27] Consistent with these bond strengths, no reaction occurs between $\mathbf{V^VO_2}$ and THF over days in the absence of O_2, as monitored by NMR or UV−vis spectroscopies. Still, an undetectable amount of reaction could be sufficient to generate the small amount of reactive species needed to initiate the autoxidation reaction.

Ultimately, all of the processes described above could be occurring during the oxidation of $\mathbf{V^{IV}O(OH)}$ by O_2. In this light, it is remarkable that $\mathbf{V^VO(O_2)}$ is generated in essentially quantitative yield, which highlights the stability of this peroxovanadium complex.

C. Reactivity with Organic Substrates. Peroxo-vanadium compounds, like related d^0 peroxo compounds of molybdenum, tungsten, and titanium, are commonly used as oxygen atom transfer reagents.[2,21,28] Still, reactions

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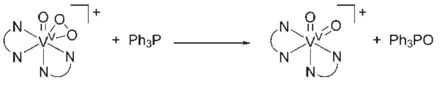
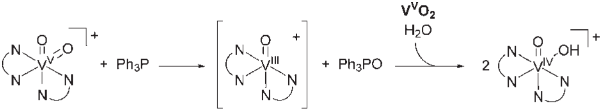
of phosphines with vanadium-oxo-peroxo complexes have only rarely been described. We have found two reports of $V(O)(O_2)L_n$ species transferring one oxygen atom to Ph_3P to give Ph_3PO and a *cis*-dioxo-vanadium product.[5,29] In the vanadium-catalyzed oxidation of triarylphosphines by H_2O_2 in acidic $MeCN/H_2O$, however, the anionic diperoxo compound $V^{V}O(O_2)_2^-$ is the reactive species, while the monoperoxo and *cis*-dioxo species do not contribute to the observed reaction rate.[30]

In the system studied here, $\mathbf{V^{V}O(O_2)}$ oxidizes Ph_3P to Ph_3PO over a few days at ambient temperatures, but the product is $\mathbf{V^{IV}O(OH)}$ not $\mathbf{V^{V}O_2}$. This is because PPh_3 reacts more quickly with $\mathbf{V^{V}O_2}$ than with the peroxo complex, as shown by independent experiments. Mostly likely, $\mathbf{V^{V}O_2}$ is deoxygenated by Ph_3P to give a transient oxovanadium(III) species which comproportionates with a second $\mathbf{V^{V}O_2}$ to give two molecules of vanadium(IV).[31] This pathway, summarized by eqs 7 and 8, accounts for the stoichiometry of 1.5 equiv of Ph_3PO per $\mathbf{V^{V}O(O_2)}$ and requires 0.5 equiv of adventitious water to form $\mathbf{V^{IV}O(OH)}$. Consistent with this suggested pathway, Zhang and Holm have reported that $V^{V}OCl_4^-$ reacts with PhP_3 to give $V^{III}Cl_4(CH_3CN)_2^-$ and Ph_3PO, and that V^{III} can accept an oxygen atom from iodosylbenzene or $V^{V}O_2Cl_2$.[32] It is interesting and unusual that $\mathbf{V^{V}O_2}$ is more reactive with Ph_3P than is $\mathbf{V^{V}O(O_2)}$, reaching completion in just a few hours instead of days.



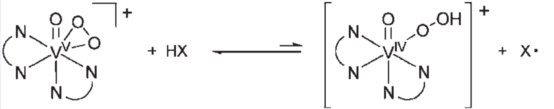
(7)



(8)

Reynolds and Butler have reported that oxygen-atom transfer reactivities of V-, Mo-, and W-peroxo compounds correlate with both the peroxo O−O stretching frequency and the λ_{max} of the peroxide-to-metal charge transfer absorption in electronic absorption spectra.[28] They note that metal monoperoxo compounds are much poorer oxygen-atom transfer reagents than metal diperoxo compounds and that V(V) peroxo complexes are generally less reactive than Mo(IV) or W(IV) peroxides. The observed O−O bond length of 1.402 Å for $[V^{V}O(O_2)(Me_2bpy)_2]BF_4$ is slightly shorter than is typical for peroxo-vanadium complexes.[3] Additionally, both the ν(O−O) of 927 cm^{-1} and the λ_{max} of 475 nm for $\mathbf{V^{V}O(O_2)}$, while typical for a vanadium(V) monoperoxo complex, are relatively high for metal-peroxo complexes. Taken together, these data suggest that the O−O bond in $\mathbf{V^{V}O(O_2)}$ is relatively strong and not very activated toward attack of substrates.

The reactions of $\mathbf{V^{V}O(O_2)}$ with the hydrogen atom donors hydroquinone and TEMPOH also occur much more slowly than analogous reactions of $\mathbf{V^{V}O_2}$, with rates that differ by an order of magnitude or more at similar concentrations.[13] We have noted previously that the dioxo compound is an unusually slow hydrogen atom acceptor,[13] so it is interesting that the oxo-peroxo complex is even less reactive. Tajika et al. have reported similar results for the reduction of tris(3-pyridyl)-methylamine oxo-peroxo-vanadium and dioxo-vanadium compounds with 2,6-di-*tert*-butylphenol and α-terpinene.[33] The first step of these reactions could be $\mathbf{V^{V}O(O_2)}$ abstracting a hydrogen atom from the substrate to give a hydroperoxo-vanadium(IV) intermediate, which is probably slow because it is significantly uphill (eq 9).[34] A similar step has been proposed in the intramolecular oxidation of isopropanol to acetone by peroxovanadium(V).[35]



(9)

Conclusions

Oxo-peroxo-vanadium(V) complexes of the formula $V^{V}O(O_2)(4,4'-R_2bpy)_2]BF_4$ (R = ^{t}Bu [$\mathbf{V^{V}O(O_2)}$], Me, or H) have been prepared by the air oxidation of vanadium(IV)-oxo-hydroxo complexes $[V^{V}O(OH)(4,4'-R_2bpy)_2]BF_4$ (R = ^{t}Bu [$\mathbf{V^{IV}O(OH)}$], Me, or H) in THF. The unusual stoichiometry, with vanadium being oxidized by 1e^- but O_2 undergoing 2e^- reduction, is accounted for by the concomitant oxidation of the THF solvent. The autoxidation of $\mathbf{V^{IV}O(OH)}$ appears to involve an initial induction period, followed by close to quantitative formation of the *cis*-dioxo-vanadium(V) species ($[V^{V}(O_2)(4,4'-^tBu_2bpy)_2]BF_4$, $\mathbf{V^{V}O_2}$) before the final $\mathbf{V^{V}O(O_2)}$ product forms. Remarkably, $\mathbf{V^{V}O_2}$ also undergoes autoxidation in THF to the peroxo complex $\mathbf{V^{V}O(O_2)}$, without change in the vanadium oxidation state. $\mathbf{V^{V}O(O_2)}$ is reduced by the weak hydrogen atom donor $\mathbf{V^{IV}O(OH)}$ to give $\mathbf{V^{V}O_2}$. $\mathbf{V^{V}O(O_2)}$ is also reduced by the organic hydrogen atom donors hydroquinone and TEMPOH, as well as the oxygen atom acceptor Ph_3P, all yielding $\mathbf{V^{IV}O(OH)}$. The peroxo species $\mathbf{V^{V}O(O_2)}$ is significantly less reactive with these organic reductants than the corresponding dioxo species $\mathbf{V^{V}O_2}$, indicating that peroxovanadium(V) species are not always as reactive as often assumed.

Experimental Section

Reagent grade chemicals were obtained from Aldrich, Eastman Organic, or Strem and used without further purification. Reagent grade solvents were purchased from Fisher Scientific or EMD chemicals. Anhydrous acetonitrile (< 10 ppm H_2O) was purchased from Honeywell Burdick & Jackson, sparged with argon, and plumbed from a steel keg

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(29) (a) Maurya, M. R.; Khurana, S.; Zhang, W.; Rehder, D. *J. Chem. Soc., Dalton Trans.* **2002**, 3015–3023. (b) Kosugi, M.; Hikichi, S.; Akita, M.; Moro-oka, Y. *J. Chem. Soc., Dalton Trans.* **1999**, 1369–1371.

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(31) The V^{III} intermediate could also react with $\mathbf{V^{V}O(O_2)}$ to give two molecules of $\mathbf{V^{V}(O)_2}$, which would then react further with PPh_3. Including this step does not affect the overall stoichiometry of 1.5 PPh_3 per $\mathbf{V^{V}O(O_2)}$.

(32) Zhang, Y.; Holm, R. H. *Inorg. Chem.* **1990**, *29*, 911–917.

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(34) Initial electron transfer is unlikely because $\mathbf{V^{V}O(O_2)}$ should be a poor one-electron oxidant: In ref 7, Tajika et al. report the V^{V}/V^{IV} $E_{1/2}$ for the very similar tris(2-pyridylmethyl)amine oxoperoxovanadium(V) complex as −1.43 V vs $Cp_2Fe^{+/0}$ in MeCN.

(35) (a) Bonchio, M.; Bortolini, O.; Carraro, M.; Conte, V.; Primon, S. *J. Inorg. Biochem.* **2000**, *80*, 191–194. (b) Bortolini, O; Conte, V.; Di Furia, F.; Modena, G. *Nouv. J. Chim.* **1985**, *9*, 147–150.

directly into the glovebox. $^{18}O_2$ (98.4% ^{18}O enrichment) gas was obtained from Isotec laboratories. Deuterated solvents and $H_2{}^{18}O$ (95% ^{18}O-enrichment) were obtained from Cambridge Isotope Laboratories. CD_2Cl_2 was dried by stirring over CaH_2 followed by vacuum transfer and stored in a dark bottle in a glovebox. CD_3CN was dried over CaH_2, vacuum transferred to P_2O_5 for 30 min, then dried over CaH_2 again, and transferred to a clean flask and stored in a glovebox. THF and THF-d_8 were stored over Na/ketyl and freshly vacuum transferred before use. TEMPOH[36] was prepared following literature procedures. Hydroquinone was recrystallized from acetonitrile.

The vanadium(IV) compounds [$V^{IV}O(OH)$(4,4′-R_2bpy)$_2$]BF_4 were prepared following the literature procedure.[13] Compounds were stored in a N_2 glovebox, and reactions were performed under N_2 using standard glovebox and Schlenk techniques. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance or DRX spectrometers (300 and 500 MHz) at ambient temperatures and are referenced to a solvent peak. Electrospray ionization mass spectra (ESI/MS) were obtained on a Bruker Esquire-LC ion trap mass spectrometer as solutions in acetonitrile, and an Agilent 5973 was used to acquire GC-MS data. IR spectra were recorded as KBr pellets or CH_2Cl_2 solutions in a cell with NaCl windows (as noted) using either a Perkin-Elmer 1720 or a Bruker Vector 33 FT-IR spectrometer. UV−vis spectra were recorded using a Hewlett-Packard 8453 spectrometer.

[$\mathbf{V^VO(O_2)}$(4,4′-^{t}Bu$_2$bpy)$_2$]BF$_4$ [$\mathbf{V^VO(O_2)}$]. $\mathbf{V^{IV}O(OH)}$ (200 mg, 0.28 mmol) was mixed with THF (200 mL) in a round-bottom flask that was sealed with a septum and vented to air with a needle. The stirred mixture changed from yellow to red in color over the course of 3 days. The solvent was then removed via rotovap and the solids redissolved in CH_2Cl_2. Dropwise addition of *n*-pentane gave a red precipitate, which was isolated by vacuum filtration and dried in vacuo to give 0.331 g (98% yield) of red-orange product. Anal. Calcd for [$\mathbf{V^VO(O_2)}$]·H_2O, $C_{36}H_{50}BF_4N_4O_4V$: C, 58.39; H, 6.81; N, 7.65. Found: C, 58.45; H, 6.57; N, 7.69. ^{1}H NMR (CD_3CN), 1st ^{t}Bu$_2$bpy ligand: δ1.24, 1.59 (each s, 9H, ^{t}Bu); 6.72, 9.64 (each d, 6 Hz, 1H, 6,6′-H); 7.10, 8.17 (each dd, 6, 2 Hz, 1H, 5,5′-H); 8.21, 8.59 (each d, 1 Hz, 1H, 3,3′-H); 2nd *t*Bu$_2$bpy ligand: 1.34, 1.60 (each s, 9H, ^{t}Bu); 7.59, 10.36 (each d, 6 Hz, 1H, 6,6′-H); 8.12, 7.43 (each dd, 6, 2 Hz, 1H, 5,5′-H); 8.43, 8.59 (each d, 2 Hz, 1H, 3,3′-H). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 30.11, 30.12, 30.35, 30.44 [$C(CH_3)_3$]; 36.24, 36.40, 36.96 (2C) [$C(CH_3)_3$]; 120.77, 122,04, 122.07, 122.85, 124.22, 125.71, 126.31, 126.62, 147.18, 148.76, 151.03, 151.22, 153.42, 153.79, 153.82, 155.33, 166.15, 167.08, 168.75 (bpy). IR-(KBr pellet, in cm^{-1}): 965 s ν(V═O), 585 cm^{-1} m and 558 w ν(V−O), 927 s ν(O−O), 1616 vs ν(C═C, C═N), 2962 vs $\nu(CH_3)$, 3121 m ν(bpy C−H). UV−vis [λ/nm, (ε/M^{-1} cm^{-1})]: 475(370), 311(24 000), 253(91 000). ESI/MS (CH_3CN): 635 [$\mathbf{V^VO(O_2)}$ − BF_4]$^+$, 619 [$\mathbf{V^VO(O_2)}$ − O − BF_4]$^+$.

[$\mathbf{V^V(^{18}O)(^{18}O_2)}$(4,4′-^{t}Bu$_2$bpy)$_2$]BF$_4$. Dry THF (10 mL, stored under N_2, over sodium benzophenone) was vacuum transferred to a 25 mL round-bottom flask containing $\mathbf{V^{IV}O(OH)}$ (15 mg, 0.021 mmol). This mixture was frozen with a liquid nitrogen/pentane bath (−131°), and the flask was exposed to ca. 1 atm of ^{18}O (1 L, 98.4 atom % ^{18}O) and sealed. After stirring for 24 h, the yellow mixture became orange. Pentane (10 mL) was vacuum transferred onto the THF mixture, and the solvents were poured off to give a red-orange solid which was dried under a vacuum. IR (KBr pellet, cm^{-1}): 920 s ν(V═^{18}O), 569 and 521 m ν(V−^{18}O), 876 s ν(O−O). IR (CH_2Cl_2 solution, cm^{-1}): 919 s ν(V═^{18}O), 874 s ν(O−O). ESI/MS (CH_3CN): 641.3 [$V^{18}O_3$(^{t}Bu$_2$bpy)$_2$]$^+$, 639.7 [$V^{18}O_2{}^{16}O$(^{t}Bu$_2$bpy)$_2$]$^+$, 623.3 [$V^{18}O_2$(^{t}Bu$_2$bpy)$_2$]$^+$, 621.9 [$V^{18}O^{16}O$(^{t}Bu$_2$bpy)$_2$]$^+$.

[$\mathbf{V^VO(O_2)}$(4,4′-Me$_2$bpy)$_2$]BF$_4$. A yellow solution of [$V^{IV}O(OH)$(4,4′-Me$_2$bpy)$_2$]BF_4 (100 mg, 0.185 mmol) in MeCN/THF (1:1 v/v, 200 mL) was stirred overnight while open to the air, turning orange. The solvent was removed by rotovap to give a red orange solid which was washed with THF and dried in vacuo (0.060 g 60% yield). Anal. Calcd for [$V^VO(O_2)$(4,4′-Me$_2$bpy)$_2$]BF_4, $C_{24}H_{24}BF_4N_4O_3V$: C, 52.01; H, 4.36; N, 10.11. Found: C, 51.86; H, 4.28; N, 9.91. ^{1}H NMR (CD_3CN): δ 2.30, 2.44, 2.74, 2.75 (each s, 3H, Me); 6.65, 7.51, 9.59, 10.30 (each d, 5.2−5.7 Hz, 1H, 6,6′-bpy H); 6.90, 7.23, 7.93, 7.98 (each d, 5.0−5.8 Hz, 1H, 5,5′-bpy H); 8.05, 8.30, 8.45, 8.47 (each s, 1H, 3,3′-bpy H). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 21.36, 21.92, 21.99 (2 C) [CH_3]; 124.14, 125.42 (2 C), 126.26, 128.05, 129.38, 129.94, 130.27, 146.94, 148.49, 150.85, 150.89, 153.03, 153.48, 153.57, 154.11, 155.00, 155.23, 156.87, 157.61 (bpy). IR(KBr pellet, cm^{-1}): 946 s ν(V═O), 923 s ν(O−O), 1619 vs ν(C═C, C═N). UV−vis [λ/nm, (ε/M^{-1} cm^{-1})]: 472(364). ESI/MS (CH_3CN): 467 [VO_3(4,4′-Me$_2$bpy)$_2$]$^+$, 451 [VO_2(4,4′-Me$_2$bpy)$_2$]$^+$.

[$\mathbf{V^VO(O_2)}$(bpy)$_2$]BF$_4$. A yellow solution of [$V^{IV}O(OH)$(bpy)$_2$]BF_4 (100 mg, 0.207 mmol) was dissolved in MeCN/THF (1:1 v/v, 200 mL) and stirred for 40 h while open to the air, turning grapefruit red in color. The solvent was removed by rotovap to give a red orange solid which was washed with THF and dried in vacuo (0.04 g, 40% yield). Anal. Calcd for [$V^VO(O_2)$(bpy)$_2$]BF_4·1/2H_2O, $C_{20}H_{17}BF_4N_4O_{3.5}V$: C, 47.37; H, 3.38; N, 11.05. Found: C, 47.66; H, 3.10; N, 11.02. ^{1}H NMR (CD_3CN): δ 6.86, 7.70, 9.81, 10.53 (each d, 4.6−5.3 Hz, 1H, 2,2′-bpy H); 7.11, 7.43, 7.91 (each t, 1H, 3,3′-bpy H); 8.14 m, 8.21 m, 8.5 d, 8.64 m, 8.59 m (2H each, remaining bpy H). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 123.69, 125.02, 125.10, 125.85, 127.65, 129.06, 129.55, 129.84, 141.59, 142.52, 143.92, 144.56, 147.66, 147.66, 149.28, 150.95, 151.71, 153.35, 153.73, 154.42, 155.38. IR (KBr pellet, cm^{-1}): 953 s ν(V═O), 923 s ν(O−O), 1607 vs ν(C═C, C═N). UV−vis [λ/nm, (ε/M^{-1} cm^{-1})]: 474 (370).

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Supporting Information Available: A CIF file for the structure of [$V^VO(O_2)(Me_2bpy)_2$]BF_4. This material is available free of charge via the Internet at http://pubs.acs.org.

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