

Oxidovanadium(V) Anchored to Silanol-Functionalized Polyoxotungstates: Molecular Models for Single-Site Silica-Supported Vanadium Catalysts

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Supporting Information

ABSTRACT: The metalation of two different types of silanoldecorated polyoxotungstates, $[XW_9O_{34-x}({}^{t}BuSiOH)_3]^{3-} (X = P, x = 0; X = Sb, x = 1)$ and $[PW_{10}O_{36}({}^{t}BuSiOH)_2]^{3-}$, by Cl₃VO or $({}^{t}PrO)_3$ VO has been achieved. The characterization of the r e s u l t i n g o x i d o v a n a d i u m (V) c o m p l e x e s $[XW_9O_{34-x}({}^{t}BuSiO)_3VO]^{3-} (X = P, 3; X = Sb, 3')$ and $[PW_{10}O_{36}({}^{t}BuSiO)_2VO({}^{t}PrO)]^{3-}$ (4) has been fully detailed, including X-ray analysis. These compounds are present in



monomeric forms and therefore represent original molecular models for tris-grafted and bis-grafted isolated $(V=O)^{3+}$ species dispersed onto silica. Their ability as precatalysts for the epoxidation of cyclic olefins and allylic alcohols with *tert*-butyl hydroperoxide (TBHP) has been studied. The results suggested that a confined tris-grafted species, such as 3 or 3', does not act as an efficient catalyst whereas a more labile bis-grafted species, such as 4, does. To gain a better understanding, we have assessed their suitability for ligand exchange with alcohols and TBHP and performed reaction progress kinetic analysis by monitoring the epoxidation of 3-methyl-2-buten-1-ol by ¹H and ⁵¹V nuclear magnetic resonance.

KEYWORDS: oxidovanadium, polyoxotungstates, silanol, site-isolated catalysts, tert-butyl hydroperoxide, epoxidation

INTRODUCTION

The fundamental understanding of the mechanisms controlling heterogeneous catalysis at a molecular level is of particular importance in an attempt to develop efficient and selective catalysts meeting the contemporary challenges of industrial processes.^{1,2} However, defining the chemical environment of an active species deposited on solid surfaces is rather difficult. This is mainly due to the effective heterogeneity and complexity of the real surface and the difficulty in unambiguously assessing the structure–activity relationship.³ While "surface organometallic chemistry"^{4–7} proved to be a relevant molecular approach^{8,9} in the rational construction of well-defined surface species, the use of molecular models can still provide valuable clues to improve our understanding of the intermediates and mechanisms occurring during heterogeneous catalysis.

Metal oxides deposited onto a large-surface area oxide represent an important class of heterogeneous catalysts in which vanadium-based species have appeared as efficient catalysts for the oxidation of hydrocarbons, alcohols, and SO₂ and more recently for the oxidative dehydrogenation of light alkanes and methanol.¹⁰ Depending on the nature of the support (montmorillonite, aluminophosphates, and silicates) and the condition of impregnation used, numerous species are discussed as active sites,^{11,12} ranging from mononuclear to dior polynuclear and also to monolayers. A discussion is also found in the literature concerning the structure of the isolated V⁵⁺ ions, tetrahedrally coordinated (V=O)³⁺ being opposed to

dioxo V(==O)₂ species, to square pyramidal or octahedral species. This ongoing argument is important because the geometry and coordination to the surface as well as surface distribution or aggregation of the metallic entities are key factors that may influence the activity and selectivity of the catalysts. This notwithstanding, true heterogeneity during oxidation catalysis in the liquid phase is also a primary issue because leaching of vanadium during the course of the catalytic reactions has been reported.^{13,14}

In this report, we describe the preparation of oxidovanadium-(V) complexes of a family of silanol-decorated polyoxotungstates that proves to be a relevant molecular model for surface vicinal silanols of dehydroxylated silica. The structures depicted in Figure 1, which have already been reported by some of us,^{15,16} exhibit a number of significant peculiarities that make them quite unique among the well-established ligand systems that are capable of mimicking a heterogeneous oxidic environment, e.g., mono- or polydentate organic silanol,^{17–20} polyhedral oligomeric silsesquioxanes (POSS),^{21–23} calix[n]arenes,^{24–29} and heteropolyanions.^{30–34} First, they display a rigid and geometrically preorganized set of silanol moieties that is well suited for the coordination and stabilization of highvalent metal ions. Second, the bulky *tert*-butyl groups at the

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Figure 1. Representations of anions 1, 1', and 2 used in this study, prepared as tetrabutylammonium salts (TBA).

silicon atoms create a sterical protection around the metal coordination site. The combination of both aspects prevents the formation of oligomers and allows the metal ion to fit in a well-defined single site. In this context, oxidovanadium(V) complexes of these silanol-functionalized polyoxotungstates are original models for isolated V⁵⁺ surface species. Hereafter, we first focus on the description of their structural analogies with silica-supported vanadium materials to validate our molecular approach to heterogeneous systems. In addition, we have assessed their suitability for ligand exchange with alcohols and *tert*-butyl hydroperoxide (TBHP) and their potential as catalysts in the epoxidation of alkenes.

RESULTS AND DISCUSSION

Synthesis. Anions 1, 1', and 2 are based on the trilacunary $[\alpha$ -A-PW₉O₃₄]⁹⁻ and $[\alpha$ -B-SbW₉O₃₃]⁹⁻ and the dilacunary $[\gamma$ -PW₁₀O₃₆]⁷⁻ Keggin-type platforms, respectively.³⁵ Compared to the closed-shell parent derivatives $[PW_{12}O_{40}]^{3-}$, the (multi)lacunary polyoxometalates (POMs) display nucleophilic oxygen atoms that open the way to their functionalization using organic electrophiles (i.e., organosilanes in this study).³⁶⁻ Indeed, the reaction of the lacunary POMs with tert-butyl trichlorosilane, under phase transfer conditions, affords (n- $Bu_4N_3[(\alpha - A - PW_9O_{34})^{(t)}BuSiOH_3]$ (TBA-1), $(n - Bu_4N_3)[(\alpha - Bu_4N_3)^{(t)}]$ B-SbW₉O₃₃)(^tBuSiOH)₃] (TBA-1'), and $(n-Bu_4N)_3[(\gamma-1)^2]$ $PW_{10}O_{36}$ (^tBuSiOH)₂ (**TBA-2**), respectively. Only minor changes to the published synthesis have been made to improve the efficiency and simplicity of the reactions. The $C_{3\nu}$ and $C_{2\nu}$ symmetries of the native POMs engaged in the reactions are retained in anions 1, 1', and 2. Moreover, it is worth emphasizing that the structure of the ^tBuSiOH groups at the "surface" of the polyoxotungstate frameworks is directly related to the symmetry of the native POMs. The rigid and 3-fold symmetric pocket generated by the ^tBuSiOH in anion 1 is quite uncommon in coordination chemistry. Such a preorganized environment is very difficult to design by organic chemistry,^{39,40} and only seldom can analogues be found in the literature, among which the polyhedral oligomeric silsesquioxane (POSS) family is probably the most relevant example. However, compared to ligand TBA-1, the POSS ligands remain flexible enough to easily promote the dimerization of coordination or organometallic compounds, and therefore, the model of site isolation at a surface (as in heterogeneous systems) is lost.^{41,42} The coordination site available in 1 is wellsuited for tetrahedral or pseudotetrahedral metal centers, and indeed, the incorporation of a $(V=O)^{3+}$ functionality is straightforward. The reaction of Cl₃VO with TBA-1 [used as such (see Experimental Section)] at room temperature in distilled acetonitrile led to the formation of the vanadium(V)

derivative $(n-Bu_4N)_3[(\alpha-A-PW_9O_{34})({}^{t}BuSiO)_3VO]$ (**TBA-3**).⁴³ The adjunction of a base is not required; nevertheless, to avoid the evolution of gaseous chlorhydric acid, compound **TBA-3** may alternatively be prepared by reacting **TBA-1** with $({}^{t}PrO)_3VO$ (see eq 1; X = Cl or ${}^{t}PrO$).

$$[PW_9O_{34}(^{t}BuSiOH)_3]^{3-} + X_3VO$$

$$\rightarrow [PW_9O_{34}(^{t}BuSiO)_3VO]^{3-} + 3HX$$
(1)

Clean reaction of (ⁱPrO)₃VO with alcohols or silanols usually requires anhydrous conditions to avoid hydrolysis of the metallic precursor. Thermogravimetric profiles of TBA-1 samples did not show any relevant mass loss below 270 °C (decomposition of ^tBuSiOH and/or TBA), whereas thermogravimetric profiles of TBA-2 samples are characterized by a first mass loss (approximately 1-2%) around 200 °C. This is attributed to the presence of water molecules (two to four molecules per 2) so that TBA-2 should be written as TBA-2. xH_2O (x = 2-4). These water molecules probably stack together forming a hydrogen bonding network on the ^tBuSiOH groups.⁴⁴ It is well-established in the chemistry of silica supports that water layers experiencing H-bonding with SiO₂ are more strongly physisorbed and heating at ~210 °C is therefore needed to remove them.45 Indeed, after TBA-2 had been heated at 210 °C for 3 h under vacuum (10^{-3} mbar), the thermogravimetric profile shows no mass loss below 270 °C. This similarity in behavior marks a certain analogy between the silanol-decorated polyoxometalates and silica. The comparison of the ¹H nuclear magnetic resonance (NMR) patterns of **TBA**-2 and its dehydrated form is also significant (Figure S1). The labile OH protons cannot be observed at room temperature (RT) because of fast exchange in solution on the NMR scale, whereas a resonance line appears at 5 ppm when ¹H NMR is performed on a dry d_3 -acetonitrile solution of the dehydrated form of TBA-2.

The reaction of $({}^{i}PrO)_{3}VO$ with dehydrated **TBA-2** in acetonitrile leads to **TBA-4** (eq 2). The release of 2 equiv of 2-propanol can be monitored by NMR spectroscopy, and the desired compound was obtained in good yields and recrystal-lized from a mixture of acetonitrile and diethyl ether.

$$[PW_{10}O_{36}(^{i}BuSiOH)_{2}]^{3-} + (^{i}PrO)_{3}VO$$

$$\rightarrow [PW_{10}O_{36}(^{i}BuSiO)_{2}VO(O^{i}Pr)]^{3-} + 2^{i}PrOH$$
(2)

Structural Characterizations. Crystals suitable for X-ray analysis were obtained for TBA-3 and TBA-4. As expected, in both cases, the complexes are present in monomeric forms. Four oxygen atoms coordinate the vanadium center tetrahedrally, and consequently, anions 3 (or 3') and 4 may be

considered as modeling species for tris-grafted (A) and bisgrafted (B) species on a siloxide surface as sketched in Chart 1.

Chart 1. Tris-Grafted (A) and Bis-Grafted (B) Species on a Siloxide Surface



The terminal V–O bond distances, 1.58(2) Å in anion 3 and 1.63(3) Å in 4, are in accordance with a $(V^V=O)^{3+}$ functionality and are comparable to those of related systems reported previously.^{12,41,46,47} As anion 3 possesses a crystallographically imposed C_3 axis running through the V metal ion and O(14), all the V–O_{Si} bonds have the same length, 1.795(9) Å (Figure 2 and Figure S2). The geometric constraint imposed



Figure 2. Crystal structure of anion 3.

by the ligand forces the vanadium center to adopt a regular tetrahedral geometry $[O(13)-V-O(13\#) = 110.3(3)^{\circ}; O(13)-V-O(14) = 108.7(3)^{\circ}]$. It is worth emphasizing the primary role of the Si(1)-O(13)-V obtuse angles observed in anion 3, 173.5(6)°. Considering the very electrophilic nature of the d^0 -vanadium center, the more obtuse the angle, the more

extended the stabilizing $O(p\pi) \rightarrow V(d\pi)$ bonding. The effect of the angle is also corroborated by the ⁵¹V chemical shifts, as shown by the comparison of the data collected for several structural models [*vide infra* (Table 1)]. The crystal structure also confirms that the bulky *tert*-butyl groups create a sterically protected well-defined single-metal site.

The crystal structure of anion 4 seems to bring up 2-fold symmetry, although this symmetry is not crystallographically imposed (no mirror plane). This symmetry breaking is probably due to a slight disorder in the organic parts. Consequently, the two V– O_{Si} bond lengths, 1.73(2) and 1.74(2) Å, are similar within experimental error. The pseudotetrahedral environment around the metal is completed by the oxido function and the remaining *i*-propoxido ligand (Figure 3 and Figure S3). The V–O(39) bond distance of



Figure 3. Crystal structure of anion 4.

1.67(2) Å appears to be slightly shorter than the V–O_{si} bond distances, which may be the consequence of the greater σ donor ability of the alkoxide ligand compared to that of the siloxide ones. It should be noted again that the Si–O–V angles in anion 4 are very obtuse, albeit smaller than in 3, 161(1)° and 163(1)°, which reflects an important O(p π) \rightarrow V(d π) stabilizing bonding [*vide infra* (Table 1)].

A thorough multinuclear NMR study (¹H, ³¹P, ²⁹Si, and ¹⁸³W) confirms the purity of **TBA-3**, **3'**, and **4**, which exhibit the expected C_3 and C_2 symmetries in solution. Of particular interest, the *tert*-butyl group at the silanol functionality is an ideal ¹H NMR probe for verifying completion of the reaction. A slight low-field shielding of the corresponding singlet is observed as a consequence of the introduction of the electron deficient (V=O)³⁺ functionality (see Experimental Section).

Table 1. Correlation between ⁵¹V NMR and the Chemical Environments in Selected Molecular Complexes

entry	complex	mean value for the Si–O–V angle (deg)	chemical shift (ppm)	ref
1	(POSS)VO (monomer)	not available	-676	41
2	(POSS)VO (dimer)	143	-710	41
3	(Ph ₃ SiO) ₃ VO	155	-725	47
4	[SbW ₉ O ₃₃ (^t BuSiO) ₃ VO] ³⁻ , 3'	152 ^{<i>a</i>}	-730	
5	$[PW_9O_{34}(^tBuSiO)_3VO]^{3-}$, 3	173.5	-800	
6	$[PW_{10}O_{36}({}^{t}BuSiO)_{2}VO({}^{i}PrO)]^{3-}$, 4	161.6	-692	

"Estimated value from a preliminary X-ray analysis of 3'. The polyoxotungstate core in anion 1', a B isomer,³⁵ provides a slightly different environment than in anion 1, an A isomer.

entry	olefin	catalyst	temp (K)	time (h)	conversion ^a (%)	selectivity of epoxide (%)
1	cis-cyclooctene	$3 (1\%)^{b}$	343	18	<5	na ^c
2		$3'(1\%)^{b}$	343	18	13	>95 ^d
3		$4 (1\%)^{b}$	343	18	21	>95
4	2-propen-1-ol	$4 (1\%)^{b}$	343	18	60	>95
5	3-methyl-2-buten-1-ol	$4 (1\%)^{b}$	343	6	>95	>95
6		$4 (1\%)^{b}$	300	6	>95	>95

Table 2. Epoxidation of Olefins (0.15 M) with TBHP (0.22 M, 1.5 equiv) in the Presence of Complexes TBA-3, 3', or 4 in Acetonitrile

^{*a*}Conversion based on NMR. ^{*b*}Catalyst loading is expressed vs the quantity of olefin. ^{*c*}The conversion is too low to ascertain the selectivity in epoxide. ^{*d*}No side products were detected by NMR.

By contrast, ³¹P NMR chemical shifts in anions 3 and 4 are poorly affected, thus indicating that the oxo anion cores remain unchanged (also correlated by the ¹⁸³W NMR analysis of TBA-3 and 3', displaying two lines in a 1:2 ratio). ⁵¹V NMR shows a broad signal centered at -800 ppm for TBA-3, -730 ppm for 3', and -692 ppm for 4. As the ⁵¹V nucleus benefits from a large shift range, its chemical shift is very sensitive to minor changes in the local environment. Of particular interest is its variation upon substitution of the siloxide ligands for the alkoxide in the metallic precursor (ⁱPrO)₃VO (-629 ppm).⁴⁸ Whereas a moderate high-field shielding (in the range of 40-80ppm for three substitutions) has been reported,49 it is important to note that in the siloxide series the ⁵¹V chemical shifts are mainly affected by the nature of the Si-O-V angle. The more obtuse the angle, the more high-field-shielded the chemical shift (entries 2-5 of Table 1). It should also be pointed out that the nature of the substituents at the silicon atom has a weak effect on the ⁵¹V chemical shift (entries 3 and 4), whereas in the case of alkoxide ligands RO⁻, bulky substituents are known to induce high-field shielding.48 With regard to compound TBA-4, the less shielded chemical shift results from the presence of a residual *i*-propoxide ligand (entry 6).

The sensitivity of the ⁵¹V chemical shift to the coordination sphere of the metal center makes ⁵¹V NMR, along with ¹H and ³¹P NMR, a useful tool for monitoring the progression of a (catalytic) reaction.

Catalytic Olefin Epoxidation. Anions 3, 3', and 4 proved to be interesting models of mononuclear V⁵⁺ surface species. We therefore studied the activity of these complexes as catalysts in the epoxidation of olefins with tert-butyl hydroperoxide (TBHP). With W^{VI}, Mo^{VI}, V^V, and Ti^{IV} catalysts, the commonly accepted mechanism is a peroxidic metal pathway^{50,51} in which (i) TBHP is activated by coordination to the metal through the oxygen distal to the ^tBu group and (ii) olefins, as nucleophiles, react with the metal-bound electrophilic oxygen in a back side approach and roughly along the axis of the oxygen-oxygen bond.^{52,53} When the substrates are allylic (or homoallylic) alcohols, the high chemoselectivity observed in the epoxide products has been explained by a mechanism that proceeds by the coordination of both reacting species, TBHP and allylic alcohol.⁵⁴ Such a mechanism requires that the precatalysts are substitution labile, and therefore, we could anticipate complex TBA-4 to be much more reactive than 3 and 3'.

We first studied the oxidation of cyclohexene and *cis*-cyclooctene (0.15 M) with TBHP (0.22 M) in the presence of a catalytic amount of complexes TBA-3, 3', and 4 (1 mol % vs olefin) in acetonitrile. At room temperature and even after a long reaction time (18–24 h), no significant conversions to epoxides were observed for any of the olefins and complexes

employed. When catalysis was conducted at 343 K (70 °C), low conversions to cyclooctene oxide were obtained (see Table 2). The better activity observed using complex TBA-4 suggested that the presence of an easy accessible coordination site is significantly important. Hence, using complex TBA-4, higher conversions were observed upon investigation of the epoxidation of the allylic alcohols 2-propen-1-ol and 3methyl-2-buten-1-ol. Full conversion was reached for the more nucleophilic olefin, and complete conversion could also be achieved at 300 K (27 °C) in 6 h (Table 2). By using the tris-siloxide complex (TBA-3'), a low conversion to epoxide was also observed for 3-methyl-2-buten-1-ol (~25% after 6 h at 300 K). Because vanadium coordination sites in anions 3 and 3' are structurally rigid, enlargement of the coordination sphere around the vanadium center (see below) is unlikely, so that the observed conversions may be attributed either to a partial decoordination from the tris-siloxide ligands or to a catalytic activity centered on the polyoxotungstic framework itself. The second point was discarded by control experiments revealing that ligands TBA-1 and 2 were not active as "catalysts". A key point was therefore to study the reactivity of complexes TBA-3, 3', and 4 toward an excess of TBHP or allylic alcohols.

When **TBA-3** and **3**' were treated with an excess of TBHP (up to 100 equiv) in dry acetonitrile- d_3 , no modification of the NMR patterns (¹H, ³¹P, and ⁵¹V NMR) was observed. A similar experiment conducted on complex **TBA-4** highlighted the release of ⁱPrOH, which is consistent with a substitution for alkyl peroxide at the vanadium center and generation of the supposed reactive alkyl peroxidic species^{55,56} $[PW_{10}O_{36}(^{t}BuSiO)_{2}VO(OO^{t}Bu)]^{3-}$ (⁵¹V NMR, δ -621):

$$[PW_{10}O_{36}(^{t}BuSiO)_{2}VO(O^{i}Pr)]^{3-} + ^{t}BuOOH$$

$$\Leftrightarrow [PW_{10}O_{36}(^{t}BuSiO)_{2}VO(OO^{t}Bu)]^{3-} + ^{i}PrOH \qquad (3)$$

The ligand exchanges at the d^0 -metal center have to proceed through a formal five-coordinate intermediate (the oxido function has been originally postulated as a possible basic site for assisting the proton transfer, but alternatively, the exchange may occur via a σ bond metathesis-type mechanism). The bidentate bis-siloxide ligand in TBA-4 displays in the solid state an $O_{\rm Si}$ -V- $O_{\rm Si}$ angle of ~113° and therefore appears to be wellsuited to accommodate a four-coordinate (pseudotetrahedral) or five-coordinate (trigonal bipyramidal) oxidovanadium species (postulated transition states in Figure 4). With regard to eq 3, it is noteworthy that the relative concentrations of both species can be assessed by ⁵¹V NMR and confirmed that TBHP has a 10-fold lower affinity for vanadium than alcohols do (K_3 ~ 0.08).⁵⁷ These experiments also pointed out that the V- $O_{\rm Si}$ bonds in anions 3 and 4 are stable toward solvolysis in the



Figure 4. Proposed chemical scheme for the reaction of 4 and analogues with TBHP and postulated transition states.

presence of hydroperoxides, as opposed to other systems (Figure 4).⁴¹

Similarly, we studied by ⁵¹V NMR the addition of an excess of 3-methyl-2-buten-1-ol to solutions of the oxidovanadium species in dry acetonitrile- d_3 . Complexes TBA-3 and 3' are almost not affected; albeit, the formation of a new vanadium species in a very low yield was revealed by the observation of a minor line at -654 and -639 ppm (Figure S4). By contrast, the addition of 3-methyl-2-buten-1-ol to a solution of TBA-4 resulted in the formation of two distinct lines in the ⁵¹V NMR spectrum corresponding to the chemical equilibrium between TBA-4 at -692 ppm and $[PW_{10}O_{36}(^{t}BuSiO)_{2}VO(OCH_{2}CH=$ $C(CH_3)_2)^{3-}$ at -678 ppm (K₄ = 0.83). The presence of an excess of olefin (100 equiv as under the catalysis conditions) shifts the equilibrium toward the new species [NMR ratio of 1:99 (see also Figure S4)]. Remarkably, ¹H and ³¹P NMR did not reveal the presence of freed ligand TBA-2, suggesting that $V-O_{Si}$ bonds in anion 4 are stable toward alcoholysis.

$$[PW_{10}O_{36}({}^{t}BuSiO)_{2}VO(O^{i}Pr)]^{3-}$$
+ (CH_{3})_{2}C=CHCH_{2}OH

$$= [PW_{10}O_{36}({}^{t}BuSiO)_{2}VO(OCH_{2}CH=C(CH_{3})_{2})]^{3-}$$
+ ${}^{i}PrOH$
(4)

To gain a better understanding of the evolution of the catalysis over time, we then decided to monitor by NMR the epoxidation of 3-methyl-2-buten-1-ol by TBHP using **TBA-3'** and **4** as (pre)catalysts. Typically, to a 2.5 mM solution of complex **TBA-3'** (or **4**) in acetonitrile- d_3 were successively added 3-methyl-2-buten-1-ol (0.25 M) and TBHP (0.27 M). Each step was followed by ¹H and ⁵¹V NMR at 300 K. These experiments brought to light the fact that the complexes display completely different kinetic profiles. When complex **TBA-4** was used as a precatalyst, the formation of epoxide started readily ($r_0 = 1.51 \text{ mM min}^{-1}$), whereas when complex **TBA-3'** was used, the formation of epoxide was not significantly observed

during a period of \sim 30 min (Figure 5 and Figure S5). The conversion into epoxide was found to be concomitant with the



Figure 5. Plot of epoxide formation vs time in the oxidation of 3methyl-2-buten-1-ol (0.25 M) by TBHP (0.27 M) in CD₃CN at 300 K, catalyzed by 1 mol % **TBA-3**' (\diamondsuit) or **TBA-4** (\bigcirc).

increase in the magnitude of the signal centered at -639 ppm (⁵¹V NMR) mentioned above. This strongly suggests that a confined tetrahedral oxidovanadium species such as that in complex TBA-3' is not active toward the epoxidation of olefins⁵⁸ and that the observed catalytic activity is most probably due to an equilibrium displacement to a partially decoordinated species in the presence of excess alcohols and TBHP. The release or leaching of vanadium in the liquid phase during oxidation reactions is well-known in heterogeneous systems. True heterogeneity has been associated with lower catalytic activity as a result of the vanadium being more strongly bonded to the support.⁵⁹ Similarly, in our systems, it should be pointed out that after a long period of catalysis the formation of (^tBuO)₃VO was clearly evidenced by ⁵¹V NMR (-672 ppm),⁴⁸ as a result of the leaching of a detectable amount of vanadium in the presence of an increasing amount of tert-butyl alcohol (produced inevitably as a byproduct).

Kinetic Analysis. Monitoring of the evolution of complex TBA-4 by ⁵¹V NMR clearly indicated two main resting states for the catalyst. Over the first 60 min, $[PW_{10}O_{36}(^{t}BuSiO)_{2}VO (OCH_2CH=C(CH_3)_2)]^{3-}$ is the dominating species, whereas in the remainder of the reaction, [PW10O36('BuSiO)2VO- $(O^{t}Bu)$]³⁻ appeared as the new dominating species (see Figure S6; a progressive enrichment in the latter species is mainly due to the increasing amount of ^{*t*}BuOH, a stronger σ donor ligand). This observation suggests that the reaction of $[PW_{10}O_{36}(^{t}BuSiO)_{2}VO(OCH_{2}CH=C(CH_{3})_{2})]^{3-}$ with TBHP is the rate-determining step, at least in the first stage of the catalysis, and that the reaction rate should depend on both concentrations. An analysis of the initial rates at different concentrations of the reagents or catalyst indicated a kinetics close to first order toward $[TBHP]_0$ and half-order toward the total vanadium concentration, [TBA-4]₀, in the range of studies (Table 3, Figure 6, and Figure S7).

Continuous monitoring of reaction progress also allows us to draw a reliable picture of the kinetics over time and most interestingly versus substrate concentration.⁶⁰ Figure 7 displays a graphical rate equation of the rate versus TBHP concentration. The straight-line relationship indicates that the epoxidation reaction exhibits a kinetics close to first-order toward [TBHP] in the range of 0.274 to 0.12 M (from 0 to 180 min) and therefore a pseudo-zero-order in [olefin] (this result

Table 3. Kinetic Data for the Vanadium-Catalyzed Epoxidation of 3-Methyl-2-buten-1-ol with TBHP in Acetonitrile at 300 K ($[olefin]_0 \approx [TBHP]_0$)

entry	$[4]_0 \times 10^{3a}$	$[TBHP]_0^a$	$r_0 \times 10^{3b}$
1	1.44	0.274	1.10
2	2.5	0.143	0.83
3		0.274	1.51
4		0.505	3.29
5		0.710	4.92
6	8.35	0.274	2.51
4.9		hn i	

^aConcentrations in moles per liter. ^bRates in molar per minute.



Figure 6. Plot of the variation of [epoxide] vs time (top) in the oxidation of 3-methyl-2-buten-1-ol with TBHP in CD₃CN at 300 K catalyzed by **TBA-4** (2.5×10^{-3} M) [[olefin]₀ \approx [TBHP]₀ = 0.143 (\Box), 0.274 (\diamondsuit), 0.505 (\bigcirc), and 0.710 M (\bigtriangleup)]. Plot of ln(r_0) vs ln([TBHP]₀) (bottom) [slope = 1.12; f(0) = -4.96; $R^2 = 0.995$].

describes a saturation kinetics in [olefin] at this first stage of the epoxidation reaction). Then the curvature in the graphical rate equation suggests a more complex relationship between the rate and the substrate concentration at longer times.⁶¹ This may be attributed to the change in the nature of the predominant resting state that becomes $[PW_{10}O_{36}(^tBuSiO)_2VO(O^tBu)]^{3-}$ (see above): the replacement of the alkoxide by the olefin may therefore impose a kinetic dependence toward [olefin] (this byproduct inhibition is known and is described well in this type of reaction).⁶² This deviation in the kinetics at a lower concentration of TBHP (thus at a higher concentration of ^tBuOH) may also be consistent with the presence of an increasing amount of released oxidovanadium species [VO-(OR)₃] that will influence the kinetics of the overall reaction.⁶³



Figure 7. Graphical rate equation (Table 3, entry 3): rate vs *tert*-butyl hydroperoxide (TBHP) concentration. The dashed-line relationship corresponds to first-order kinetics in the concentration of substrate.

CONCLUSIONS

Silanol-decorated $[XW_9O_{34-x}(^tBuSiOH)_3]^{3-}$ (X = P, x = 0; X = Sb, x = 1 and $[PW_{10}O_{36}(^{t}BuSiOH)_{2}]^{3-}$ polyoxotungstates have been used as ligands in an elegant approach to model surface silanols. The preparation and structural characterization of oxidovanadium (V) complexes (n- $Bu_4N_3[XW_9O_{34-x}(^tBuSiO)_3VO]$ (for TBA-3, X = P and x = 0; for TBA-3', X = Sb and x = 1) and (n- $Bu_4N)_3[PW_{10}O_{36}(^tBuSiO)_2VO(^iPrO)]$ (TBA-4) have been fully detailed, including X-ray analysis. These complexes provide interesting models for tris- and bis-grafted single-site silica-supported vanadium catalysts, respectively. The kinetic study of the epoxidation reaction of alkenes and allylic alcohols by tert-butyl hydroperoxide clearly confirmed that an isolated tetrahedral $(V=O)^{3+}$ complex is not an active species. Instead, a partial decoordination appears to be a prerequisite for allowing the oxidation to take place. This point has been inferred from ⁵¹V NMR spectroscopy and from the much higher catalytic efficiency displayed by complex TBA-4, a homogeneous analogue to bipodal vanadium oxido alkoxide surface species. The originality of our models stems from the ability of lacunary polyoxotungstates to generate a rigid and geometrically preorganized set of silanol moieties. The bulky tert-butyl groups at the silicon atoms create a sterical protection that ensures the oxidovanadium will fit in a well-defined single site, a fundamental condition for developing a relevant molecular approach to oxo surfaces. Major applications of polyoxotungstates in catalysis rely on their thermal and oxidative robustness that makes them efficient and recyclable catalysts with a low environmental impact, and we are therefore confident that the further preparation, structures, and catalytic properties of metallic complexes based on ligands 1 and 2 will also provide helpful information concerning the formation and analysis of surface species.

EXPERIMENTAL SECTION

General Procedures. The lacunary polyoxotungstates, $K_9[\alpha$ -A-PW₉O₃₄],⁶⁴ Na₉[α -B-SbW₉O₃₃],⁶⁴ and Cs₇[γ -PW₁₀O₃₆],^{65,66} and their silanol derivatives, (n-Bu₄N)₃[(α -A-PW₉O₃₄)(^tBuSiOH)₃] (**TBA-1**),⁶⁷ (n-Bu₄N)₃[(α -B-SbW₉O₃₃)-(^tBuSiOH)₃] (**TBA-1**),⁶⁸ and (n-Bu₄N)₃[(α -PW₁₀O₃₆)-(^tBuSiOH)₂] (**TBA-2**),¹⁶ respectively, were prepared as reported in the literature. All manipulations were conducted under an inert atmosphere using standard Schlenk techniques. *tert*-Butyl hydroperoxide (TBHP, 5.5 M in decane), Cl₃VO, and

(ⁱPrO)₃VO were purchased from Aldrich or Strem and used as received. ¹H NMR and ³¹P{¹H} NMR spectra were recorded at room temperature in 5 mm outside diameter tubes on a Bruker AvanceII 300 spectrometer equipped with a QNP probehead or on a Bruker AvanceIII 600 spectrometer equipped with a BBFO probehead. ⁵¹V (157.9 MHz) NMR and ¹⁸³W (25 MHz) NMR spectra were recorded on a Bruker AvanceIII 600 spectrometer equipped with a low-frequency BBO probehead at room temperature in 10 mm outside diameter tubes. For ¹H, chemical shifts are referenced with respect to tetramethylsilane by using the solvent signals as a secondary standard. For ${}^{31}P{}^{1}H$, chemical shifts were measured by the substitution method and are given with respect to 85% H₃PO₄. With regard to ¹⁸³W NMR, the chemical shifts are given with respect to a 2 M Na₂WO₄ aqueous solution and were determined by the substitution method using a saturated D₂O solution of tungstosilicic acid $H_4SiW_{12}O_{40}$ as a secondary standard (δ -103.8). Elemental analyses were performed by the Service de microanalyses of the ICSN-CNRS (Gif-sur-Yvette, France).

Dehydration of TBA₃[PW₁₀O₃₆(^tBuSiOH)₂] (TBA-2). Samples of TBA₃[PW₁₀O₃₆(^tBuSiOH)₂] were dehydrated by being heated at 210 °C for 3 h under dynamic vacuum (10⁻³ mbar) and stored under an inert atmosphere before use: ¹H NMR (CD₃CN, 300.13 MHz, 300 K) δ 5 (s, 2H, SiOH), 3.2 (m, 24 H, NCH₂ TBA), 1.6 (m, 24 H, CH₂ TBA), 1.4 (m, 24 H, CH₂ TBA), 1.1 (s, 18 H, CH₃ ^tBuSi), 1.0 (t, 36 H, CH₃ TBA); ³¹P NMR (CD₃CN, 121.5 MHz, 300 K) δ – 14.9.

Synthesis of TBA₃[PW₉O₃₄(^tBuSiO)₃VO] (TBA-3). One gram (0.306 mmol) of $TBA_3[PW_9O_{34}(^{t}BuSiOH)_3]$ (1) was placed in a Schlenk tube, and under an argon atmosphere, freshly distilled acetonitrile (20 mL) was added. The solution was cooled to 0 °C, and 32 μ L (0.337 mmol) of Cl₃VO was added. The resulting reddish solution was allowed to warm to room temperature to give a colorless solution. After being stirred at room temperature overnight, the solution was lavered with diethyl ether to afford crystallization of the compound. The crystals were filtered off, washed with diethyl ether, and dried under vacuum: 730 mg (72% yield); ¹H NMR (CD₃CN, 300.13 MHz, 300 K) δ 3.16 (m, 24 H, NCH₂ TBA), 1.66 (m, 24 H, NCH₂CH₂ TBA), 1.43 (sext, ${}^{2}J_{H,H} = 7.2$ Hz; 24 H, CH_2CH_3 TBA), 1.17 (s, 27 H, CH_3 ^tBuSi), 1.0 (t, ² $J_{H,H}$ = 7.2 Hz; 36 H, CH₂CH₃ TBA); {¹H}³¹P NMR (CD₃CN, 121.5 MHz, 300 K) δ -15.2; {¹H}¹³C NMR (CD₃CN, 75.5 MHz, 300 K) δ 66.3 (C(CH₃)₃), 59.4 (NCH₂), 27.1 (C(CH₃)₃), 24.4 (NCH₂CH₂), 20.4 (CH₂CH₃), 14.0 (CH₂CH₃); ¹⁸³W NMR (CH₃CN/CD₃CN, 12.5 MHz, 300 K) δ -80.7 (3W), -157.9 (6W); ²⁹Si NMR (CD₃CN, 59.6 MHz, 300 K) δ –55 ($\omega_{1/2}$ = 80 Hz, broad signal due to the coupling with quadripolar $\frac{51}{V}$; ⁵¹V NMR (CD₃CN, 78.9 MHz, 300 K) δ – 800 ($\omega_{1/2}$ = 240 Hz). Elemental analysis calcd (%) for C₆₀H₁₃₅N₃O₃₈PSi₃VW₉ (3327.4): C, 21.66; H, 4.09; N, 1.26. Found: C, 21.71; H, 3.99; N, 1.21.

TBA₃[SbW₉O₃₃(^tBuSiO)₃VO] (TBA-3'). The title compound was prepared following the same procedure as for the synthesis of **TBA-3**: ¹H NMR (CD₃CN, 300.13 MHz, 300 K) δ 3.12 (m, 24 H, NCH₂ TBA), 1.63 (m, 24 H, NCH₂CH₂ TBA), 1.38 (sext, ²J_{H,H} = 7.2 Hz; 24 H, CH₂CH₃ TBA), 1.25 (s, 27 H, CH₃ ^tBuSi), 0.98 (t, ²J_{H,H} = 7.2 Hz; 36 H, CH₂CH₃ TBA); ²⁹Si NMR (CD₃CN, 59.6 MHz, 300 K) δ -51 ($\omega_{1/2}$ = 100 Hz, broad signal due to the coupling with quadripolar ⁵¹V); ¹⁸³W (CD₃CN, 12.5 MHz, 300 K) δ -117 (3W), -119.2 (6W); ⁵¹V NMR (CD₃CN, 78.9 MHz, 300 K) δ -730 ($\omega_{1/2}$ = 200 Hz).

Synthesis of TBA₃[PW₁₀O₃₆(^tBuSiO)₂VO(^tPrO)] (TBA-4). Dehydrated $TBA_3[PW_{10}O_{36}(^{t}BuSiOH)_2]$ (2) (402 mg, 0.12 mmol) was placed in a Schlenk tube. Under an argon atmosphere, freshly distilled acetonitrile (4 mL) was then added followed by 30 μ L (0.13 mmol) of (ⁱPrO)₃VO at room temperature and the solution was stirred overnight. The resulting greenish solution was then layered by 11 mL of freshly distilled diethyl ether. After 4 days, the formation of crystals was observed, the solution was removed, and the crystalline solid was washed with diethyl ether and dried under vacuum: 153 mg (37% yield); ¹H NMR (CD₃CN, 300.13 MHz, 300 K) δ 5.68 (sept, ³J = 6 Hz; 1H, (CH₃)₂CHO-V), 3.17 (m, 24 H, NCH₂ TBA), 1.66 (m, 24 H, CH₂ TBA), 1.53 (d, ${}^{3}J$ = 6 Hz; 6H, (CH₃)₂CHO-V), 1.43 (m, 24 H, CH₂ TBA), 1.15 (s, 18 H, CH₃ ^tBuSi), 1.02 (t, 36 H, CH₃ TBA); ³¹P NMR (CD₃CN, 121.5 MHz, 300 K) δ -15.05 (s); ⁵¹V NMR (CD₃CN, 105.2 MHz, 300 K) δ –692 ($\omega_{1/2}$ = 60 Hz). Elemental analysis calcd (%) for C₅₉H₁₃₃N₃O₄₀PSi₂VW₁₀ (3501.2): C, 20.24; H, 3.83; N, 1.20. Found: C, 20.13; H, 3.80; N, 1.14.

X-ray Crystallography. A single crystal of each compound was selected, mounted onto a cryoloop, and transferred in a cold nitrogen gas stream. Intensity data were collected with a Bruker Kappa-APEXII diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Data collections were performed with the APEX2 suite (Bruker). Unit cell parameter refinement, integration, and data reduction were performed with SAINT (Bruker). SADABS (Bruker) was used for scaling and multiscan absorption corrections.

In the WinGX suite of programs,⁶⁹ the structures were determined with either Sir92⁷⁰ or SUPERFLIP⁷¹ and refined by full-matrix least-squares methods using SHELXL-14.⁷² Non-hydrogen atoms were essentially refined anisotropically. In **TBA-3**, disordered carbon atoms of *tert*-butyl moieties were refined isotropically. In **TBA-4**, ADPs of TBA cations were restrained to be similar to or to follow a rigid bond condition. Some C–C distances were also restrained to be similar in the latter compound. Hydrogen atoms were placed at calculated positions.

CCDC 1414350 and 1414351 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Catalytic Olefin Epoxidation. To a screw-capped Schlenk tube (equipped with a rotaflo-type valve) were added under argon the catalyst (50 μ mol), acetonitrile (3 mL), the olefin (0.5 mmol, 0.15 M), and *tert*-butyl hydroperoxide (0.75 mmol, 0.22 M). The mixture was stirred while being heated at the desired temperature (300 or 343 K) for 18 h. Dilution by diethyl ether gave a turbid suspension from which the solid may be taken off (by filtration or centrifugation). Conversions were assigned by NMR analysis.

Monitoring by NMR. A screw-capped 5 mm outside diameter NMR tube under argon was charged with complex TBA-4 (4.8 mg, 1.37 μ mol) and dry acetonitrile- d_3 (0.5 mL). 3-Methyl-2-buten-1-ol (17 μ L, 166 μ mol) and TBHP (5.5 M in decane, 30 μ L, 165 μ mol) were successively added to the mixture. Each step was monitored at 300 K by ¹H, ³¹P, and ⁵¹V NMR on a Bruker AvanceIII 600 spectrometer equipped with a BBFO probehead. The acquiring parameters (relaxation delays) have been optimized to ensure an accurate integration measurement. The NMR data set (integral measurements) was fitted to a polynomial function to generate a full profile.

The functions were then differentiated to obtain rate versus time data (see Figure S8).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01878.

Crystal data, data collection, and structure refinement details for TBA-3 (\mbox{CIF})

Crystal data, data collection, and structure refinement details for TBA-4 (CIF)

¹H NMR patterns of compound **TBA-2** before and after thermal treatment, evolution of the ⁵¹V NMR of compounds **TBA-3**' and **TBA-4** in the presence of 3methyl-2-buten-1-ol, close-up of the plot of epoxide formation of 3-methyl-2-buten-1-ol by TBHP catalyzed by **TBA-3**' and **TBA-4**, time evolution of the ⁵¹V NMR of compound **TBA-4** during the catalysis, graphical rate equations, and kinetic data for the epoxidation of 3methyl-2-buten-1-ol with TBHP using VO(ⁱPrO)₃ as a precatalyst (PDF)

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Notes

The authors declare no competing financial interest.

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