Catalytic Epoxidation

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Polyoxovanadometalate-Catalyzed Selective Epoxidation of Alkenes with Hydrogen Peroxide**

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Vanadium is an important element in biology, inorganic chemistry, and organic syntheses,[1–8] and can heterogeneously or homogenously catalyze selective oxidation reactions of alkanes, alkenes, aromatic compounds, alcohols, halides, etc.[1–4,7–14] While homogenous oxidation catalysis by mono- and divanadium complexes has extensively been studied, the oxidation catalysis by bis(μ-hydroxo)-bridged divanadium compounds is scarcely known.[1–8,15,16] In addition, even monovanadium complexes cannot efficiently catalyze the epoxidation of alkenes by a green oxidant such as H_2O_2 because of a contribution from the radical mechanism; for example, the oxidation of cyclohexene by H_2O_2 in the presence of vanadium-based catalysts proceeds mainly at the allylic position.[9–14] Moreover, the efficiency of H_2O_2 utilization is intrinsically low.[9–14] Therefore the vanadium-catalyzed, H_2O_2-based epoxidation of alkenes with high selectivity to the epoxide and high efficiency of H_2O_2 utilization is currently not possible, although it is well known that other transition metals such as tungsten, manganese, and iron show high activity and selectivity.[17–20]

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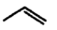
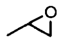
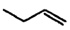
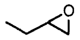
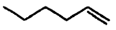
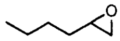
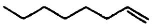
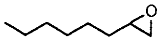
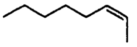
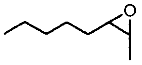
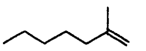
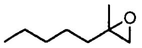
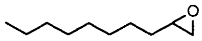
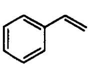
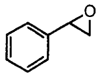
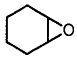
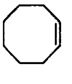
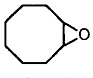
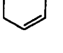
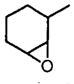
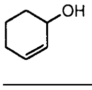
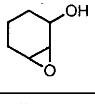
The catalytic function of polyoxometalates has attracted much attention because the ability to design catalytically active sites means that their redox and acidic properties can be controlled at the atomic or molecular levels.[21–28] Recently, various efficient catalytic systems for H_2O_2-based epoxidation by polyoxometalates have been developed with peroxotungstates or -molybdates as catalyst precursors or with transition-metal-substituted polyoxometalates. However, these require either an excess of H_2O_2 with respect to the alkene or an excess of alkene with respect to H_2O_2 to attain a high yield of epoxide or high efficiency of H_2O_2 utilization.[29] Herein, we report that $[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$ (**1**), which has a $\{VO\text{-}(\mu\text{-}OH)_2\text{-}VO\}$ core, can catalyze the epoxidation of alkenes in the presence of only one equivalent of H_2O_2 with a high yield of epoxide and high efficiency of H_2O_2 use. Notably, this system shows unique stereospecificity, diastereoselectivity, and regioselectivity that are quite different from those reported for the epoxidation systems based on $[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$.[30,31] Furthermore, we have investigated the active site of **1** and the active species for the present epoxidation on the basis of various physicochemical characterizations.

First, we examined the scope of the present epoxidation with the tetra-*n*-butylammonium salt of **1** (TBA-**1**), various kinds of alkenes, and with only one equivalent of H_2O_2 (except for gaseous alkenes; Table 1). Under the present reaction conditions, the amounts of allylic oxidation products and glycols produced by hydrolysis were negligible in all cases. The epoxidation did not proceed at all in the absence of catalyst, and no epoxidation was observed with *tert*-butylhydroperoxide (TBHP) as the oxidant. Nonactivated aliphatic terminal C_3–C_{10} alkenes, including propene, could be transformed into the corresponding epoxides with ≥99% selectivity and ≥87% efficiency of H_2O_2 utilization. A larger-scale reaction (50-fold scale-up) for 1-octene showed the same results as the small-scale experiments (99% selectivity to 1,2-epoxyoctane, 93% yield determined by GC, and 86% yield of isolated product). The reaction rate increased with an increase in the reaction temperature, and the TOF reached as high as 38 h^{-1} at 313 K whilst maintaining the selectivity for 1,2-epoxyoctane as high as >99%, although the efficiency of H_2O_2 utilization decreased slightly from 93% (293 K) to 85% (313 K). Acid-sensitive styrene was epoxidized to give styrene oxide as the sole product. Also, the catalytic epoxidation of cyclic alkenes such as cyclohexene and cyclooctene proceeded efficiently to afford the corresponding epoxides in high yields.

Table 1: Epoxidation of various monoalkenes catalyzed by TBA-**1**.[a]

Substrate	Product	Yield [%]	Selectivity [%]	E_{ox} [%][b]
 [c]		87	99	87
 [d]		91	99	91
		92	99	92
		93	99	93
		90	99 (only *cis*)	90
		88	98	90
		93	99	93
		88	99	88
		90	99	92
		93	99	93
		91	97 (*syn*/*anti* = 5/95)	91
		87	95 (*syn*/*anti* = 12/88)	91

[a] Reaction conditions: alkene (33.3 mM), TBA-**1** (1.67 mM), H_2O_2 (30% aq., 33.3 mM), and CH_3CN/*t*BuOH (1.5/1.5 mL) at 293 K for 24 h. Yields and selectivities were determined by gas chromatography or ^1H NMR spectroscopy using an internal standard technique and are based on alkenes. [b] $E_{ox}(H_2O_2$ efficiency) = [products (mol)/consumed H_2O_2 (mol)] × 100. [c] Propene pressure 6 atm. [d] 1-Butene pressure 3 atm.

The epoxidation of *cis*- and *trans*-2-octene gave *cis*-2,3-epoxyoctane (90% yield; Table 1) and *trans*-2,3-epoxyoctane (6% yield), respectively; the configuration around the C=C moieties is retained in these epoxides. Moreover, for the competitive epoxidation of *cis*- and *trans*-2-octenes (100 μmol each, the other conditions were the same as in Table 1), the initial rates for the epoxidation were 0.32 and 0.001 mM min^{-1}, respectively. The ratio of the formation rate of *cis*-2,3-epoxyoctane to that of the *trans* isomer is more than 3×10^2, which is much larger than the ratios (1.3–11.5) reported for other stereospecific epoxidation systems (see Supporting Information). For competitive epoxidation of *cis*- and *trans*-2-octenes, the yields of *cis*-2,3-epoxyoctane and the *trans* isomer (based on H_2O_2), even after 24 h, were 91 and 2%, respectively. The epoxidation of 3-substituted cyclohexenes, such as 3-methyl-1-cyclohexene and 2-cyclohexen-1-ol, showed an unusual diastereoselectivity: the corresponding epoxides are formed highly diastereoselectively with the oxirane ring *trans* to the substituents (*anti* configuration; Table 1 and Tables S2 and S3 in the Supporting Information).

Further, the more accessible, but less nucleophilic double bonds in nonconjugated dienes such as *trans*-1,4-hexadiene, (*R*)-(+)-limonene, 7-methyl-1,6-octadiene, and 1-methyl-1,4-cyclohexadiene were epoxidized in high yields in a highly regioselective manner, as shown in Table 2. The values of [less-substituted epoxide]/[total epoxides] (≥0.88) are much higher than those reported for the other epoxidation systems (Tables S4–S7 in the Supporting Information). As far as we know, such unique stereospecificity, diastereoselectivity, and regioselectivity have never been reported for **1**.

The relative reactivity (rate) of a series of C_8 alkenes decreased in the order of 2-methyl-1-heptene (1.1) > 1-octene (1.0 taken as unity) > *cis*-2-octene (0.87) > 2-methyl-2-heptene (0.03) > *trans*-2-octene (<0.01) (see Table S8 in the Supporting Information). This order is not consistent with that of the π(C=C) HOMO energies of C_8 alkenes because they decrease with an increase in the number of alkyl substituents in alkenes, as reported previously.[30] Therefore, the inconsistency between the ordering of the π(C=C)

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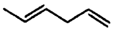
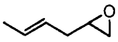
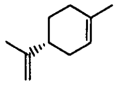
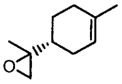
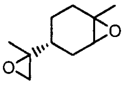
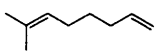
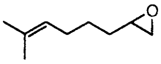
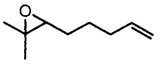
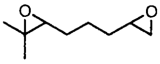
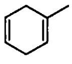
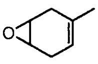
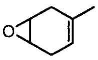
Table 2: Epoxidation of various nonconjugated dienes catalyzed by TBA-**1**.[a]

Substrate	Product	Yield [%]	[less-substituted epoxide]/[total epoxides]	E_{ox} [%][b]
		91	> 0.99	91
		89	0.99	91
		1		
		77	0.93	87
		5		
		4		
		71	0.88	81
		5		

[a], [b] See footnotes to Table 1.

HOMO energies and the reactivities should be caused by the steric constraints of the active site of **1**, that is, an active oxygen species formed by the reaction of **1** with H_2O_2 is embedded in the polyoxometalate framework and thus a sterically hindered C=C double bond cannot easily approach the site.

The mono- and trivanadium-substituted compounds $[\alpha\text{-SiVW}_{11}O_{40}]^{5-}$ and $[\alpha\text{-1,2,3-SiV}_3W_9O_{40}]^{7-}$ are inactive for the epoxidation under the present conditions, which suggests that the V–O–W and V=O centers are not the active sites. The fully occupied silicotungstate $[\gamma\text{-SiW}_{12}O_{40}]^{4-}$, which has the same structure as **1**, is also inactive, which suggests that the tungsten atoms in **1** are not the active sites. The regioselectivity of the catalytic epoxidation of nonconjugated dienes by **1** is quite different from that by $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$ (Tables S4–S7 in the Supporting Information), which shows that the catalytically active site (species) of **1** is different from that of $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$.

In addition, we confirmed by in situ IR and NMR measurements that tungstate compounds such as $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$ and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ are not formed during the catalysis. The ^{51}V NMR spectrum of the recovered catalyst in CD_3CN shows a line at $\delta = -564$ ppm ($\Delta\nu_{1/2} = 125$ Hz) and the ^{183}W NMR spectrum in CD_3CN shows three lines at $\delta = -84$ ($\Delta\nu_{1/2} = 9.9$ Hz), -97 ($\Delta\nu_{1/2} = 2.3$ Hz), and -131 ppm ($\Delta\nu_{1/2} = 1.6$ Hz) with an integrated intensity ratio of 2:1:2, in agreement with the γ-Keggin framework. Signals due to tungstate compounds such as $[\alpha\text{-SiW}_{12}O_{40}]^{4-}$, $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$, $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$, and $[H_nWO_2(O_2)_2]^{(2-n)-}$ were not observed. The IR and UV/Vis spectra of the catalyst recovered after the completion of the epoxidation were the same as those of the fresh one, which also suggests the maintenance of the γ-Keggin framework of **1**.

All these facts strongly indicate that the {VO-(μ-OH)$_2$-VO} core is preserved in the cluster framework of **1** during the catalytic process and that tungstate compounds are not the true catalytically active species in the present epoxidation. The fact that the regioselectivities for nonconjugated dienes with **1** are different from those with $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$ and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ also support this idea.

Next, the reactivity of **1** with H_2O_2 was investigated. The cold-spray ionization mass spectrum (CSI-MS) of TBA-**1** in 1,2-$C_2H_4Cl_2$ shows the most intense parent-ion peak (centered at *m/z* 3337.9) with an isotopic distribution (Figure 1a and Supporting Information) that agrees with the pattern calculated for $[(TBA)_3H_2SiV_2W_{10}O_{40}]^-$ (Figure 1b and Supporting Information). Upon the addition of 350 equiv of H_2O_2, a new peak centered at *m/z* (3337.9 + 16) appeared (Figure 1c) which agrees with the pattern calculated for $[(TBA)_3HSiV_2W_{10}O_{39}(OOH)]^-$ (Figure 1d).

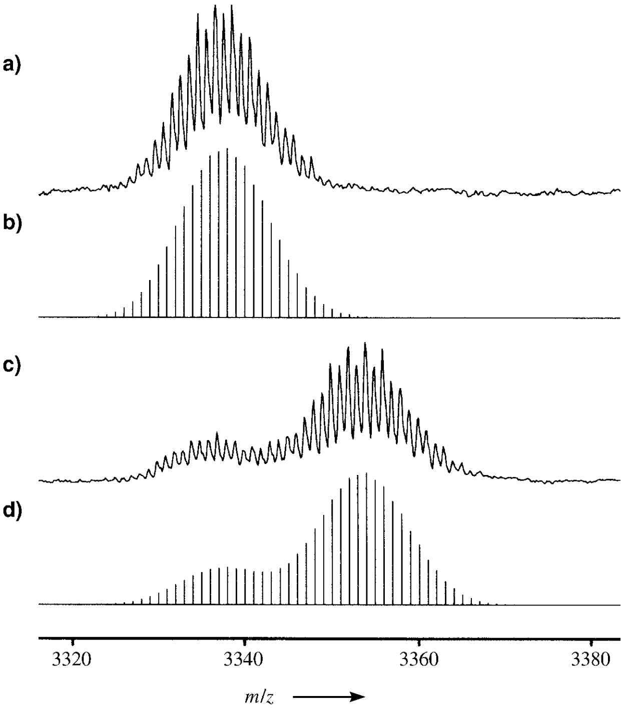


Figure 1. CSI-MS (anion mode, *m/z* 3300–3400) of a) TBA-**1** (0.14 mM) in 1,2-$C_2H_4Cl_2$ and c) TBA-**1** (0.14 mM) in 1,2-$C_2H_4Cl_2$ treated with 350 equiv of H_2O_2 (96% aqueous solution) with respect to TBA-**1** (253 K, 2 h). The lines in (b) are the pattern calculated for $[(TBA)_3H_2SiV_2W_{10}O_{40}]^-$ and the lines in (d) are the pattern calculated for a mixture of $[(TBA)_3H_2SiV_2W_{10}O_{40}]^-$ (22%) and $[(TBA)_3HSiV_2W_{10}O_{39}(OOH)]^-$ (78%). The small increase in the content of $[(TBA)_3H_2SiV_2W_{10}O_{40}]^-$ in comparison with those of Figures 2–4 is probably caused by a slight increase in the temperature at the inlet of the injection port of the spectrometer.

The ^{1}H NMR spectrum of **1** (2.5 mM) in 1,2-$C_2D_4Cl_2$ at 253 K shows a signal at $\delta = 4.80$ ppm due to the hydroxy proton of the {VO-(μ-OH)$_2$-VO} core in **1**. Upon the addition of 20 equiv of H_2O_2, two signals appear at $\delta = 5.10$ and

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9.45 ppm with an intensity ratio of 1:1, and the intensity of the signal at $\delta = 4.80$ ppm has greatly decreased (by (93 ± 1) %) after 2 h, although the sum of the three signal intensities remains almost constant (Figure 2). A similar lower-field shift of the hydroxy proton signal from $\delta = 5.10$ to $\delta = 5.18$ ppm has been observed upon the formation of $[\gamma\text{-}1,2\text{-}SiV_2W_{10}O_{38}(\mu\text{-}OH)(\mu\text{-}OCH_3)]^{4-}$ in CD_3CN.[32] The chemical shift of $\delta = 9.45$ ppm is close to those of other hydroperoxide species such as H_2O_2 ($\delta = 8.74$ ppm), *t*BuOOH ($\delta = 8.84$ ppm), and $PhC(CH_3)_2OOH$ ($\delta = 8.95$ ppm).

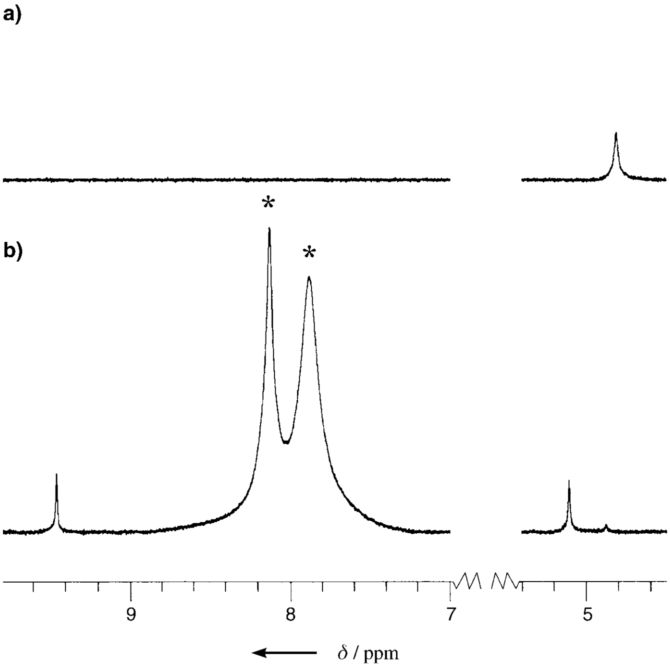

Figure 2. ^1H NMR spectra of a) TBA-**1** (2.5 mM) in $1,2\text{-}C_2D_4Cl_2$ and b) TBA-**1** (2.5 mM) in $1,2\text{-}C_2D_4Cl_2$ treated with 20 equiv of H_2O_2 (95 % aqueous solution) with respect to TBA-**1** at 253 K for 2 h. The asterisks indicate the signals of H_2O_2 in the organic and aqueous phases.

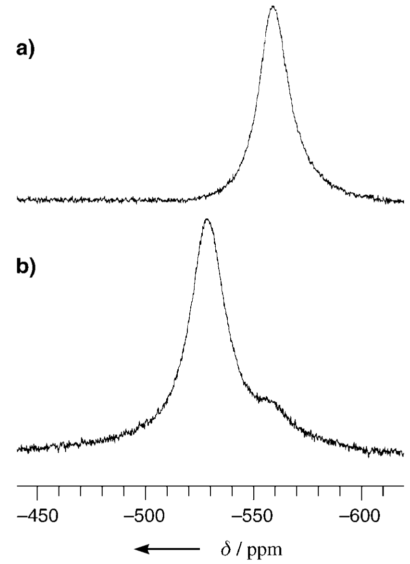

Figure 3. ^{51}V NMR spectra of the same samples as for Figure 2.

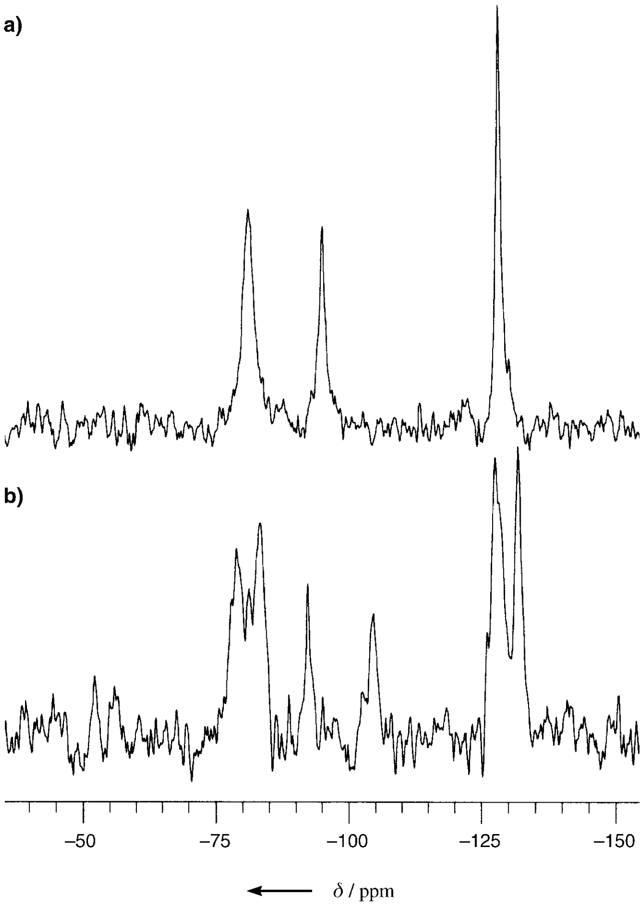

Figure 4. ^{183}W NMR spectra of a) TDA-**1** (0.1 M) in $1,2\text{-}C_2D_4Cl_2$ and (b) TDA-**1** (0.1 M) in $1,2\text{-}C_2D_4Cl_2$ treated with 15 equiv of H_2O_2 (95 % aqueous solution) with respect to TDA-**1** at 253 K for 2 h. TDA = *n*-decylammonium.

One new ^{51}V NMR signal appears at $\delta = -530$ ppm in $1,2\text{-}C_2D_4Cl_2$ upon the addition of H_2O_2, and the intensity of the signal of **1** at $\delta = -562$ ppm has greatly decreased (by (93 ± 1) %) after 2 h, although, again, the sum of the two signal intensities remains almost constant (Figure 3). Six new ^{183}W NMR signals appear at $\delta = -79$, −83, −92, −104, −127, and −132 ppm with an intensity ratio of 2:2:1:1:2:2, in $1,2\text{-}C_2D_4Cl_2$ upon the addition of 15 equiv of H_2O_2, and the signals at $\delta = -81$, −95, and −128 ppm due to **1** have almost completely disappeared after 2 h, although the sum of the nine signal intensities remains almost constant (Figure 4). A quantitative analysis of the ^1H, ^{51}V, and ^{183}W NMR data gives an atomic ratio of $H(\delta{=}5.10\text{ ppm}):H(9.45):V(-530):W(-79):W(-83):W(-92):W(-104):W(-127):W(-132)$ of 1:1:2:2:2:1:1:2:2.

The ^{183}W NMR spectral pattern depends on the structure and symmetry of the anion. The anion **1** has C_{2v} symmetry and shows three signals with intensities of 2:1:2. The reaction of **1** with H_2O_2 lowers or does not change the symmetry of the anion, and there are five possibilities for the symmetry of the resulting compound: 1) C_2, 2) C_s with a symmetry plane containing two vanadium atoms, 3) C_s with a symmetry plane containing two V–O–V bridging oxygen atoms, 4) C_1, and 5) C_{2v}. After the treatment of **1** with H_2O_2, six ^{183}W NMR signals are observed with an intensity ratio of 2:2:1:1:2:2; only case (3) can explain the observed ^{183}W NMR spectrum.[33] The ^{1}H NMR spectrum shows two signals at $\delta = 5.14$ (1 H) and 9.45 ppm (1 H). These two protons must exist in the symmetry plane, which favors the C_s symmetry. The ^{51}V NMR spectrum shows one signal. Therefore, the NMR data indicate the formation of a {VO-(μ-OH)(μ-OOH)-VO} species.

The chemical shifts of the ^{51}V and ^{183}W NMR signals are also in agreement with this idea: the oxo→peroxo transformation for complexes of ^{51}V, ^{95}Mo, and ^{183}W leads to significant upfield shifts in the NMR signals (see Table S11 in the Supporting Information). On the other hand, the oxo→hydroperoxo transformation from $H_xMoO_2(O_2)_2^{(2-x)-}$ ($0 \leq x \leq 1$) to $[MoO(O_2)_2OOH]_2^{2-}$ produces a 15–30 ppm downfield shift in the ^{95}Mo signals;[34] no ^{51}V NMR data have been reported for the oxo→hydroperoxo transformation as far as we know. In the present case, a downfield shift of 32 ppm is observed for the ^{51}V NMR signal after the treatment of **1** with H_2O_2. Such a downfield shift is in accordance with the oxo→hydroperoxo transformation. These NMR and CSI-MS data strongly suggest that the {VO-(μ-OH)$_2$-VO} core in **1** reacts with H_2O_2 to form a {VO-(μ-OH)(μ-OOH)-VO} species.

The methanol monoester of **1** (**2**) was easily formed by the dehydrative condensation between the hydroxy group in **1** and methanol (equilibrium constant 75).[32] No diester was formed even in the presence of an excess of methanol. The anionic cluster **2** retains the γ-Keggin structure with the two vanadium atoms bridged by one protonated oxygen atom and one methoxy group.[32] Therefore, the dehydrative condensation between **1** and H_2O_2 to form the hydroperoxo complex should proceed as reported for bis(μ-hydroxo) complexes of the first row transition metals.[35] When one proton in the {VO-(μ-OH)$_2$-VO} site in **1** was removed by titration with 1 equivalent of nBu_4NOH with respect to **1**, neither esterification of **1** with methanol nor its epoxidation with H_2O_2 proceeded. All these results indicate that the {VO-(μ-OH)$_2$-VO} core in **1** is the active site that forms {VO-(μ-OH)(μ-OOH)-VO} species for the epoxidation of olefins with H_2O_2, according to Equation (1) with R = OH, CH_3.

$$\begin{aligned}&[\gamma\text{-1,2-}H_2SiV_2W_{10}O_{40}]^{4-} + ROH\\ &\rightarrow [\gamma\text{-1,2-}SiV_2W_{10}O_{38}(\mu\text{-}OH)(\mu\text{-}OR)]^{4-} + H_2O\end{aligned} \tag{1}$$

As has been reported previously,[32] the esterification of the {VO-(μ-OH)$_2$-VO} core in **1** with alcohols is sterically controlled: the esters of primary alcohols with a bulky substituent, such as neopentyl alcohol, or of secondary and tertiary alcohols are hardly formed (equilibrium constant < 0.02) because of the steric repulsion from the polyoxometalate framework. For the same reason, no reaction of **1** with TBHP occurs. Thus, the hydroperoxo group in the possible intermediate $[\gamma\text{-1,2-}SiV_2W_{10}O_{38}(\mu\text{-}OH)(\mu\text{-}OOH)]^{4-}$ may also be sterically hindered, which could explain the unique stereospecificity, diastereoselectivity, and regioselectivity in the epoxidation catalysis (Figure S3 in the Supporting Information).

Experimental Section

An aqueous solution of $[\gamma\text{-1,2-}H_2SiV_2W_{10}O_{40}]^{4-}$ was prepared according to reference [36], and the anion was isolated as the tetra-*n*-butylammonium salt (TBA-**1**): $K_8[\gamma\text{-}SiW_{10}O_{36}]\cdot 12\,H_2O$[37] (8 g, 2.7 mmol) was quickly dissolved in 1 M HCl (28 mL), $NaVO_3$ (0.5 M, 11 mL, 5.5 mmol) was added, and the mixture was gently stirred for 5 min. The solution was filtered and $[(n\text{-}C_4H_9)_4N]Br$ (8 g, 25 mmol) added in a single step. The resulting yellow precipitate was collected by filtration and then washed with a large amount of water (300 mL). The crude product was purified twice by precipitation (addition of 1 L of H_2O to an acetonitrile solution of TBA-**1** (50 mL)). Analytically pure TBA-**1** was obtained as a pale-yellow powder. Yield: 7.43 g (76 %). Anal. calcd. for $[(C_4H_9)_4N]_4[\gamma\text{-1,2-}H_2SiV_2W_{10}O_{40}]\cdot H_2O$: C 21.4, H 4.15, N 1.56, Si 0.78, V 2.83, W 51.1, H_2O 0.50; found: C 21.4, H 3.91, N 1.59, Si 0.79, V 2.88, W 51.2, H_2O 0.50. ^{51}V NMR (CD_3CN): An intense signal at $\delta = -563.6$ ppm ($\Delta\nu_{1/2} = 133$ Hz) attributed to two equivalent vanadium atoms is observed. ^{183}W NMR (CD_3CN): $\delta = -82.2$ ($\Delta\nu_{1/2} = 9.6$ Hz), -95.6 ($\Delta\nu_{1/2} = 2.5$ Hz), and -129.7 ppm ($\Delta\nu_{1/2} = 2.9$ Hz) with an integrated intensity ratio of 2:1:2. ^{29}Si NMR (CD_3CN): $\delta = -84.0$ ppm ($\Delta\nu_{1/2} = 2.0$ Hz). The UV/Vis spectrum (in CH_3CN) shows shoulder bands at 240 ($\varepsilon = 36\,000\ M^{-1}cm^{-1}$), 285 (24 000), and 350 nm (5900), characteristic of the γ-Keggin structure.[38,39] IR (KBr): $\tilde{\nu} = 1151, 1106, 1057, 1004, 995, 966, 915, 904, 875, 840, 790, 691, 550, 519, 482, 457, 405\ cm^{-1}$.

The epoxidation of gaseous substrates (propene and 1-butene) was carried out in a Teflon-coated autoclave; a glass-tube reactor was used for the other substrates. The epoxidation was carried out as follows: catalyst (1.67 mM), CH_3CN/tBuOH (1.5/1.5 mL), H_2O_2 (30 % aq., 33.3 mM), and substrate (propene, 6 atm; 1-butene, 1 atm; others, 33.3 mM) were charged in the reaction vessel. The reaction was carried out at (293 ± 0.2) K. The reaction solution was sampled periodically and analyzed by GC in combination with mass spectrometry. The products were identified by comparing their mass and NMR spectra with those of authentic samples. The carbon balance in each experiment was in the range of 95–100 %. The amount of H_2O_2 remaining after the reaction was analyzed by Ce^{4+}/Ce^{3+} titration.[40] After the reaction, the catalyst was recovered by evaporating the reaction mixture to dryness, followed by washing with tBuOH and n-hexane. TOF values were estimated from the initial rates below 10 % conversion of H_2O_2.

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