

# Olefin Epoxidation with Hydrogen Peroxide Catalyzed by Lacunary Polyoxometalate $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$

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**Abstract:** The tetra-*n*-butylammonium (TBA) salt of the divacant Keggin-type polyoxometalate  $[\text{TBA}]_4[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]$  (**I**) catalyzes the oxygen-transfer reactions of olefins, allylic alcohols, and sulfides with 30% aqueous hydrogen peroxide. The negative Hammett  $\rho^+$  (−0.99) for the competitive oxidation of *p*-substituted styrenes and the low value of (nucleophilic oxidation)/(total oxidation),  $X_{\text{SO}}=0.04$ , for **I**-catalyzed oxidation of thianthrene 5-oxide (SSO) reveals that a strongly electrophilic oxidant species is formed on **I**. The preferential formation of *trans*-epoxide during epoxidation of 3-methyl-

1-cyclohexene demonstrates the steric constraints of the active site of **I**. The **I**-catalyzed epoxidation proceeds with an induction period that disappears upon treatment of **I** with hydrogen peroxide. <sup>29</sup>Si and <sup>183</sup>W NMR spectroscopy and CSI mass spectrometry show that reaction of **I** with excess hydrogen peroxide leads to fast formation of a diperoxo species,  $[\text{TBA}]_4[\gamma\text{-SiW}_{10}\text{O}_{32}(\text{O}_2)_2]$  (**II**), with retention of a  $\gamma$ -Keggin type

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structure. Whereas the isolated compound **II** is inactive for stoichiometric epoxidation of cyclooctene, epoxidation with **II** does proceed in the presence of hydrogen peroxide. The reaction of **II** with hydrogen peroxide would form a reactive species (**III**), and this step corresponds to the induction period observed in the catalytic epoxidation. The steric and electronic characters of **III** are the same as those for the catalytic epoxidation by **I**. Kinetic, spectroscopic, and mechanistic investigations show that the present epoxidation proceeds via **III**.

## Introduction

Selective oxygen transfer to olefins remains an important research area in industrial and synthetic chemistry, because epoxides are widely used as epoxy resins, paints, surfactants, and intermediates in various organic syntheses.<sup>[1]</sup> A catalytic epoxidation system that uses hydrogen peroxide as a terminal oxidant offers advantages because hydrogen peroxide can oxidize organic compounds with relatively high atom ef-

iciency and theoretically generates only water as a co-product. Consequently, a number of metal-catalyzed epoxidation systems with hydrogen peroxide have been developed.<sup>[2]</sup>

Polyoxometalates (POMs) are molecular metal–oxygen clusters with discrete structures. The chemistry of POMs has attracted much attention, and the versatility and accessibility of POMs have led to many applications in various areas.<sup>[3]</sup> The oxidation and acid functions of POMs are of great importance in catalysis, because the redox and acidic properties can be controlled at atomic or molecular levels.<sup>[4]</sup> Various epoxidation reactions with hydrogen peroxide catalyzed by POMs have been developed.<sup>[5]</sup> We have made a preliminary report on an efficient, simple route for the epoxidation of various olefins with hydrogen peroxide catalyzed by a divacant lacunary silicotungstate,  $[\text{TBA}]_4[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]$  (**I**) (Figure 1).<sup>[6]</sup> Although **I** showed specific reactivity and selectivity for the epoxidation, the mechanism is still unclear.

The activation of hydroperoxides, including alkyl hydroperoxides and hydrogen peroxide, by d<sup>0</sup> transition metals has received much attention, because Group IV–VII metals have been employed for industrial olefin epoxidation with

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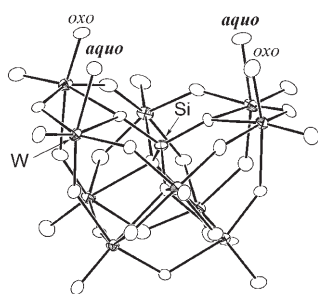


Figure 1. Molecular structure of the anionic part of **I**.

organic hydroperoxides (the Halcon–Arco process).<sup>[2d]</sup> It has been accepted for the activation of alkyl hydroperoxide that the oxygen-transfer reaction to olefin proceeds via an intermediate that has  $\eta^2$  coordination of the peroxide to the Lewis acid metal center, which has been characterized structurally in some cases.<sup>[7–11]</sup> Recent studies using molybdenum–diperoxo complexes with *tert*-butyl hydroperoxide (TBHP) show that the activation of TBHP by the peroxy complexes with a Lewis acid is a key step in the catalytic cycle.<sup>[9]</sup> For the activation of hydrogen peroxide with  $d^0$  transition metals, various modes of peroxy species such as  $M(\eta^2-O_2)$ ,<sup>[7,8,12]</sup>  $M(\mu-\eta^2-\eta^1-O_2)$ ,<sup>[13]</sup> and  $M(OOH)$ <sup>[14]</sup> have been postulated as active species for olefin epoxidation, depending on the metals and their structures.<sup>[2]</sup>

In this paper, we report full details of the catalytic performance of **I** in the oxidation of various olefins and sulfides with hydrogen peroxide, and investigate kinetic and mechanistic aspects of the **I**-catalyzed epoxidation system, including the electronic and steric natures of the active oxygen species.

## Results and Discussion

**Oxidation of olefins and sulfides with hydrogen peroxide catalyzed by **I**:** Epoxidation of 1-octene was carried out with polyoxometalates and peroxotungstates under various conditions (Table S1). Compound **I** exhibited the highest activity among the catalysts tested (entry 1). Epoxidation did not proceed without catalysts (entry 2). TBA salts of fully occupied and the other lacunary polyoxometalates were completely inactive (entries 3–6). Epoxidation with organic hydroperoxides such as TBHP and cumene hydroperoxide (CHP) did not proceed (entries 9 and 10), in accord with the report that tungsten compounds are not active for oxidation with organic hydroperoxides.<sup>[15]</sup>

Acetonitrile was the most effective solvent (entry 1). Biphasic benzonitrile/1,2-dichloroethane systems and homogeneous *n*-butyronitrile/acetone systems gave 1,2-epoxyoctane selectively in moderate to good yields (entries 11–14). Chloroform, benzene, *n*-hexane, methanol, and *tert*-butanol, in which **I** was not soluble, were poor solvents (entries 15–19). *N,N*-Dimethylformamide and dimethyl sulfoxide were also poor solvents although **I** was soluble in them (entries 20 and 21). The addition of only two equivalents imidazole or

pyridine with respect to **I** strongly inhibited the epoxidation in acetonitrile (entries 22 and 23).

High yields and efficiency were achieved by using hydrogen peroxide for **I**-catalyzed epoxidation of various terminal, internal, and cyclic olefins (Table 1, entries 1–21). High yields and selectivity for the epoxidation of *cis*-2-octene, *cis*-3-octene, and cyclooctene were observed under stoichiometric conditions (that is,  $H_2O_2/olefin/I = 125:125:1$ ; Table 1, entries 7, 9, and 20). *cis*- $\beta$ -Methylstyrene was converted to *cis*- $\beta$ -methylstyrene oxide selectively, while a small amount of benzaldehyde was formed by C=C bond cleavage for epoxidation of styrene (entries 23 and 22).<sup>[16]</sup> For the nonconjugated dienes, **I** showed a specific regioselectivity different from those of peroxotungstates and stoichiometric oxidants such as dimethyldioxirane and *m*-chloroperoxybenzoic acid (entries 24–28).<sup>[6b]</sup> For epoxidation of 1-methyl-1,4-cyclohexadiene, the ratio of 4,5-epoxide to total epoxides was 0.89 and the more accessible but less nucleophilic double bond was much more selectively epoxidized (entry 24). On the other hand, epoxidation of 7-methyl-1,6-octadiene and 4-vinyl-1-cyclohexene took place mainly at the electron-rich double bonds (entries 27 and 28). These trends of regioselectivity for **I** are in good agreement with the results of competitive epoxidation of  $C_6$  olefins that have similar alkyl substituents to the corresponding dienes (Table S2). For epoxidation of primary allylic alcohols, the corresponding epoxy alcohols were obtained selectively with small amounts of  $\alpha,\beta$ -unsaturated aldehydes (entries 29–31). Geraniol was epoxidized regioselectively at the electron-deficient allylic 2,3 double bond without formation of the 6,7-epoxy alcohol (entry 32). On the other hand, geranyl acetate was epoxidized selectively at the electron-rich double bond to give the 6,7-epoxide (entry 33). Similar regioselectivities for geraniol and geranyl acetate were observed for epoxidation with hydrogen peroxide catalyzed by the peroxotungstates.<sup>[17,18]</sup>

The present system also catalyzed the oxidation of sulfides with hydrogen peroxide (Table 2). It was confirmed that oxidation of alkyl sulfide (methyl *n*-octyl sulfide) and aryl sulfide (1-methoxy-4-(methylthio)benzene) did not proceed at all without catalysts under the present conditions. Thioanisole was oxidized with high selectivity and efficiency by using hydrogen peroxide, even under stoichiometric conditions (Table 2, entry 2). Various sulfides were oxidized selectively to the corresponding sulfoxides with high efficiency by using hydrogen peroxide (entries 1–14).<sup>[19]</sup> The reaction rates were affected by the electronic effects of the substituents on the aromatic rings of aryl sulfides (entries 1–10).<sup>[20]</sup> Not only aryl sulfides but also alkyl ones could be oxidized to the corresponding sulfoxides in excellent yields (entries 11 and 12).

### Electronic and steric character of the active oxygen species:

Although the intramolecular regioselectivity for epoxidation of nonconjugated dienes that have two electronically and sterically inequivalent double bonds provides much information on the active oxygen species,<sup>[5,6b]</sup> it can only estimate the effect of both the steric and the electronic character of

Table 1. Epoxidation of various olefins with hydrogen peroxide catalyzed by **I**.<sup>[a]</sup>

	Substrate	<i>t</i> [h]	Yield [%]	Selectivity to epoxide [%]	H <sub>2</sub> O <sub>2</sub> efficiency [%]
1 <sup>[b]</sup>	propylene	8	90	> 99	> 99
2 <sup>[b]</sup>	1-butene	8	88	99	> 99
3 <sup>[b]</sup>	1,3-butadiene	9	91	99	99
4	1-hexene	12	80	99	94
5	1-octene	10	90	> 99	> 99
6 <sup>[c]</sup>	<i>cis</i> -2-octene	3	> 99	> 99	> 99
7 <sup>[c,d]</sup>	<i>cis</i> -2-octene	10	77	95	89
8 <sup>[c]</sup>	<i>cis</i> -3-octene	3	> 99	> 99	> 99
9 <sup>[c,d]</sup>	<i>cis</i> -3-octene	10	87	98	99
10 <sup>[c]</sup>	<i>cis</i> -2-hexene	2	> 99	> 99	> 99
11 <sup>[e]</sup>	<i>trans</i> -2-octene	14	91	> 99	99
12	2-methyl-1-pentene	10	98	99	98
13	2-methyl-2-pentene	8	> 99	> 99	> 99
14	cyclopentene	3	> 99	> 99	> 99
15	cyclohexene	6	84	> 99	> 99
16	cycloheptene	4	> 99	> 99	> 99
17	1-methylcyclohexene	4	95	> 99	99
18 <sup>[f]</sup>	2-norbornene	4	> 99	99	> 99
19	cyclooctene	2	99	> 99	> 99
20 <sup>[d]</sup>	cyclooctene	24	99	99	99
21 <sup>[g]</sup>	cyclododecene	4	97	> 99	> 99
22 <sup>[h]</sup>	styrene	12	70	84	98
23 <sup>[c]</sup>	<i>cis</i> - $\beta$ -methylstyrene	4	> 99	98	99
24 <sup>[i]</sup>	1-methyl-1,4-cyclohexadiene	4	> 99	93	> 99
25 <sup>[j]</sup>	<i>trans</i> -1,4-hexadiene	7	70	> 99	81
26 <sup>[g,k]</sup>	( <i>R</i> )-(+)-limonene	7	91	97	93
27 <sup>[l]</sup>	7-methyl-1,6-octadiene	6	94	> 99	> 99
28 <sup>[m]</sup>	4-vinyl-1-cyclohexene	4	98	99	98
29 <sup>[n]</sup>	2-buten-1-ol	14	99	88	99
30 <sup>[o]</sup>	3-methyl-2-buten-1-ol	5	> 99	89	> 99
31 <sup>[p]</sup>	2-methyl-2-propen-1-ol	13	93	88	94
32 <sup>[q]</sup>	geraniol	4	97	89	97
33 <sup>[r]</sup>	geranyl acetate	8	98	> 99	98

[a] Reaction conditions, unless otherwise stated: **I** (8  $\mu$ mol), substrate (5 mmol), 30% aqueous hydrogen peroxide (1 mmol), acetonitrile (6 mL), 305 K. Yield (%) = products (mol)/H<sub>2</sub>O<sub>2</sub> used (mol)  $\times$  100. H<sub>2</sub>O<sub>2</sub> efficiency (%) = products (mol)/consumed H<sub>2</sub>O<sub>2</sub> (mol)  $\times$  100. [b] Propylene (6 atm), 1-butene (3 atm), 1,3-butadiene (2.5 atm). [c] Only *cis*-epoxide. [d] Olefin (1 mmol). [e] Only *trans*-epoxide. [f] Only *exo*-epoxide. [g] Acetonitrile (9 mL). [h] Benzaldehyde (select. 16%) was formed. [i] 4,5-Epoxide/(total epoxide) = 0.89. Toluene (select. 7%) was formed as a by-product. [j] 1,2-Epoxide/(total epoxide) = 0.61. [k] 8,9-Epoxide/(total epoxide) = 0.38. [l] 1,2-Epoxide/(total epoxide) = 0.17. [m] (Terminal epoxide)/(total epoxide) = 0.04. [n] Substrate: *cis/trans* = 11:89; epoxy alcohol: *cis/trans* = 30:70. 2-Butenal (select. 12%) was formed as a by-product. [o] 3-Methyl-2-butenal (select. 11%) was formed as a by-product. [p] 2-Methyl-2-propenal (select. 12%) was formed as a by-product. [q] Only 2,3-epoxide was formed. Geraniol (select. 11%) was formed as a by-product. [r] 2,3-Epoxide/(total epoxide) = 0.12.

Table 2. Oxidation of various sulfides with hydrogen peroxide catalyzed by **I**.<sup>[a]</sup>

	Sulfide	<i>t</i> [h]	Yield [%]	Selectivity to sulfoxide [%]	H <sub>2</sub> O <sub>2</sub> efficiency [%]
1	thioanisole	1	98	> 99	98
2 <sup>[b]</sup>	thioanisole	2	97	95	99
3	4-(methylthio)toluene	1	> 99	> 99	> 99
4	4-chlorophenyl methyl sulfide	1	97	> 99	97
5	4-bromothioanisole	1	> 99	> 99	> 99
6	1-methoxy-4-(methylthio)benzene	1	98	> 99	98
7	4-fluorothioanisole	1	95	> 99	95
8	4-(methylthio)acetophenone	1	> 99	> 99	> 99
9	4-(methylthio)benzotrile	1	> 99	> 99	> 99
10 <sup>[c]</sup>	4-nitrothioanisole	1	93	> 99	> 99
11	ethyl <i>n</i> -propyl sulfide	2	84	> 99	> 99
12	methyl <i>n</i> -octyl sulfide	2	94	> 99	> 99
13	ethyl phenyl sulfide	2	94	> 99	94
14	benzyl methyl sulfide	2	98	> 99	98

[a] Reaction conditions, unless otherwise stated: **I** (1.6  $\mu$ mol), substrate (1 mmol), 30% aqueous hydrogen peroxide (0.2 mmol), acetonitrile (1.2 mL), 305 K. Yield and H<sub>2</sub>O<sub>2</sub> efficiency calculated as in Table 1. [b] Olefin (1 mmol). [c] Acetonitrile (2.4 mL).

the active oxygen species together. We have therefore assessed the steric and electronic characters of the active oxygen species separately.

First, the electronic characters of the active oxygen species were examined. The good linearity of Hammett plots ( $\log(k_X/k_H)$  versus  $\sigma^+$ ) for the competitive oxidation of styrene and *p*-substituted styrenes (Figure 2) suggests that the present epoxidation proceeds by means of a single mecha-

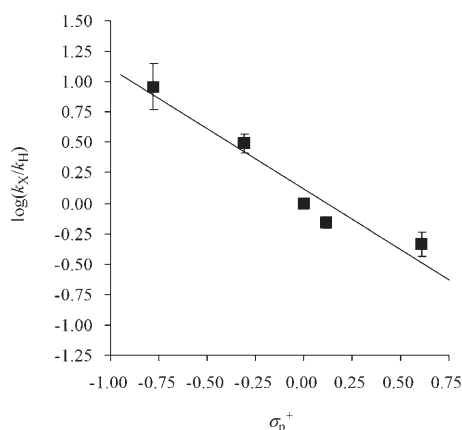


Figure 2. Hammett plot for the competitive oxidation of styrene and *p*-substituted styrenes. Reaction rates were estimated by the conversion of substrates. Reaction conditions: styrene (2.5 mmol), *p*-substituted styrene (2.5 mmol), **I** (8.0  $\mu$ mol), 30% aqueous hydrogen peroxide (1.0 mmol), CH<sub>3</sub>CN (6 mL), 305 K. Slope =  $-0.99$  ( $R^2 = 0.93$ ).

nism. The negative  $\rho^+$  ( $-0.99$ ) agrees with the formation of an electrophilic oxygen species on **I**.<sup>[21]</sup> The electronic character of this species was examined further by using SSO as a probe for the electronic character of the oxidant (Table 3).<sup>[22]</sup> The oxidation did not proceed without **I** under the present conditions (entry 4). The results for oxidation of SSO by the tungsten-based complexes showed relatively low  $X_{SO}$  values ( $X_{SO} = (\text{nucleophilic oxidation}) / (\text{total oxidation}) = (\text{SSO}_2 + \text{SOSO}_2) / (\text{SSO}_2 + \text{SOSO}_2 + 2\text{SOSO}_2)$ ) and the sulfide site of SSO was much more selectively oxidized (entries 1–3), demonstrating the electrophilic nature of the active oxygen species. The  $X_{SO}$  value for each run in Table 3 changed little during the oxidation of SSO (for example, its value for **I** was within the range of 0.04–0.06 through-

out the 220 min reaction). The  $X_{SO}$  value obtained with **I** (0.04) was lower than those of the tetra(*n*-hexyl)ammonium (THA) salt of  $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$  (0.18) and the dodecyltrimethylammonium (DTMA) salt of  $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$  (0.35), suggesting that the active oxygen species on **I** is the most electrophilic among these tungstates under the present conditions.<sup>[23]</sup>

The 3-alkyl-substituted cyclohexenes provide a quantitative measure of purely steric effects for the epoxidations, since electronic interactions between the C=C double bond and the allylic substituents are not possible.<sup>[24]</sup> The *trans* diastereoselectivity (*trans/cis* = 81:19) for the epoxidation of 3-methyl-1-cyclohexene by **I** was higher than those by  $[\text{THA}]_3[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]$  (56:44) and  $[\text{DTMA}]_2[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]$  (55:45) [Eq. (1)]. The *trans/cis* ratio for **I** (81:19) was lower than that of Ti- $\beta$  (92:8) with the steric constraints due to the narrow channels,<sup>[24a]</sup> and much higher than those of CH<sub>3</sub>ReO<sub>3</sub>/UHP (49:51),<sup>[24b]</sup> Ti-MCM-41/TBHP (58:42),<sup>[24a]</sup> Ti-ITQ-2/TBHP (61:39),<sup>[24a]</sup> and of stoichiometric reagents *m*-CPBA (48:52)<sup>[24c]</sup> and dimethyldioxirane (52:48).<sup>[24d]</sup>

These results for the competitive oxidation of *p*-substituted styrenes, oxidation of SSO, and epoxidation of 3-methyl-1-cyclohexene suggest that a strong electrophilic oxidant species with steric hindrance is formed by the reaction of **I** with hydrogen peroxide. The specific regioselectivity for epoxidation of nonconjugated dienes with hydrogen peroxide

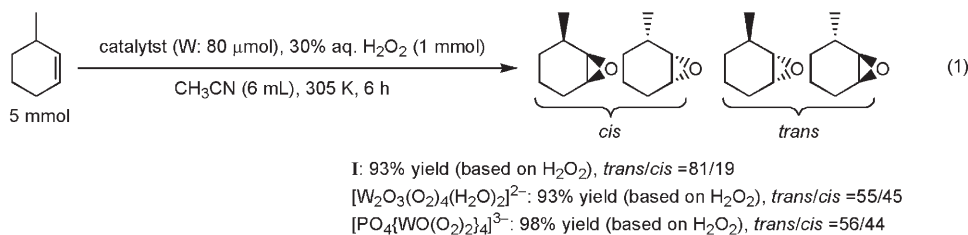


Table 3. Oxidation of thianthrene 5-oxide (SSO).<sup>[a]</sup>

Catalyst	<i>t</i> [min]	Yield [%]	Selectivity [%]				<i>cis/trans</i>	$X_{SO}$
			SSO <sub>2</sub>	<i>cis</i> -SOSO <sub>2</sub>	<i>trans</i> -SOSO <sub>2</sub>	SOSO <sub>2</sub>		
1 <b>I</b>	220	96	2	16	80	1	17:83	0.04
2 <sup>[b]</sup> $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$	60	80	23	18	40	19	30:70	0.35
3 <sup>[c]</sup> $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$	40	>99	8	37	43	12	47:53	0.18
4 none	1440	<1	–	–	–	–	–	–
5 <sup>[d]</sup> <i>m</i> -CPBA	<20	>99	13	29	58	<1	33:67	0.13

[a] Reaction conditions, unless otherwise stated: catalyst (2  $\mu$ mol), SSO (200  $\mu$ mol), acetonitrile (5 mL), 30% aqueous hydrogen peroxide (50  $\mu$ mol), 298 K. Yield and selectivity were determined by HPLC analysis with an internal standard technique. Yield [%] = products [mol]/initial oxidant [mol]  $\times$  100.  $X_{SO} = (\text{SSO}_2 \text{ [mol]} + \text{SOSO}_2 \text{ [mol]}) / (\text{SOSO}_2 \text{ [mol]} + \text{SSO}_2 \text{ [mol]} + 2 \times \text{SOSO}_2 \text{ [mol]})$ . [b] Dodecyltrimethylammonium salt (10  $\mu$ mol). [c] Tetra-*n*-hexylammonium salt (5  $\mu$ mol). [d] *m*-CPBA (50  $\mu$ mol), SSO (200  $\mu$ mol), chloroform (5 mL), 298 K.

by **I** probably reflects their electronic and steric characters.<sup>[6b]</sup>

**Reactivity of **I** with hydrogen peroxide:** The time course for the present epoxidation of cyclooctene with hydrogen peroxide catalyzed by **I** showed an induction period of approximately 60 min (Figure 3) that disappeared upon pretreat-

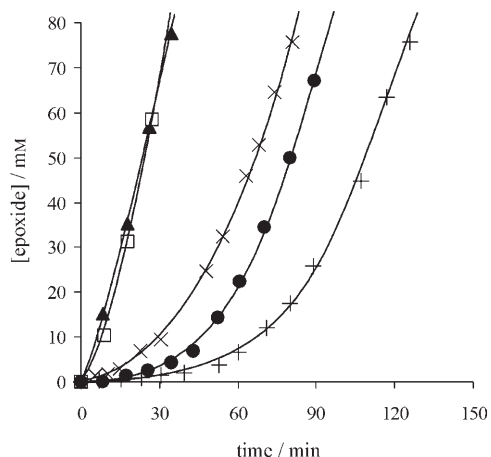


Figure 3. Reaction profiles for the epoxidation of cyclooctene with 30% aqueous hydrogen peroxide catalyzed by **I**: [**I**] (1.18 mM), [cyclooctene] (0.74 M), [H<sub>2</sub>O<sub>2</sub>] (0.15 M), [H<sub>2</sub>O] (0.65 M), acetonitrile (6 mL), reaction temperature 305 K; ●: Without pretreatment; ▲: with pretreatment by 30% aqueous hydrogen peroxide before addition of cyclooctene for 60 min at 305 K; +: with pretreatment by cyclooctene before addition of 30% aqueous hydrogen peroxide for 60 min at 305 K; □: with addition of HClO<sub>4</sub> (0.30 mM) without pretreatment; ×: using **II** (1.18 mM) instead of **I** without pretreatment.

ment of **I** with hydrogen peroxide (60 min), whereas an induction period of approximately 80 min was still observed for the pretreatment with cyclooctene. It was concluded that the induction period was caused by the reaction of **I** with hydrogen peroxide to form catalytically active species. The  $\gamma$ -Keggin structure of **I** during the catalysis was stable, as previously reported,<sup>[6,25]</sup> showing that the induction period is not due to structural degradation and that the present catalysis does not originate from the tungstates formed by the decomposition of **I**. On the other hand, a mixture of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, hydrogen peroxide, and an olefin resulted in the decomposition of [PW<sub>12</sub>O<sub>40</sub>]<sup>3-</sup>.<sup>[26]</sup>

Next, the reactivity of **I** with hydrogen peroxide was investigated. One new <sup>29</sup>Si NMR signal appeared at  $\delta = -84.1$  ppm upon addition of ten equivalents hydrogen peroxide with respect to **I** (30% aqueous solution), showing the formation of a single species (**II**) (Figure 4b). The chemical shift of **II** differed from that of **I** ( $\delta = -83.5$  ppm, Figure 4a). The <sup>183</sup>W NMR spectrum of **I** with C<sub>2</sub> symmetry showed five signals at  $\delta = -95.7$ ,  $-98.9$ ,  $-118.2$ ,  $-119.6$ , and  $-195.7$  ppm, intensity ratio 1:1:1:1:1, respectively (Figure 5a). Upon addition of hydrogen peroxide, five new <sup>183</sup>W NMR signals appeared at  $\delta = -125.9$ ,  $-135.4$ ,  $-155.3$ ,  $-219.7$ , and  $-554.6$  ppm, intensity ratio 1:1:1:1:1, respectively (Fig-

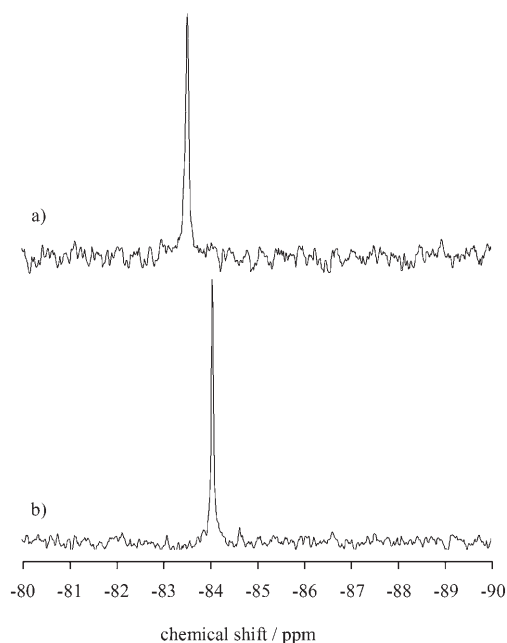


Figure 4. <sup>29</sup>Si NMR spectra of a) **I** in CD<sub>3</sub>CN/[D<sub>6</sub>]DMSO (2:1, v/v) at 298 K; b) **II** in CD<sub>3</sub>CN at 263 K [after treatment of **I** with hydrogen peroxide (10 equiv relative to **I**; 30% aqueous solution) at 263 K for 3 h].

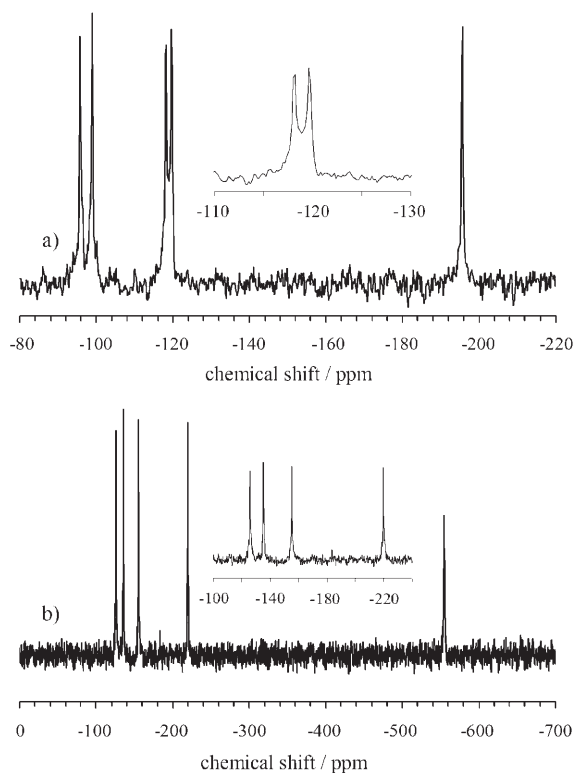


Figure 5. <sup>183</sup>W NMR spectra of a) **I** in CD<sub>3</sub>CN/[D<sub>6</sub>]DMSO (2:1, v/v) at 298 K; b) **II** in CD<sub>3</sub>CN at 263 K [after treatment with H<sub>2</sub>O<sub>2</sub> (10 equiv relative to **I**; 30% aqueous solution) at 263 K for 3 h].

ure 5b). It has been reported for molybdenum and tungsten compounds that the coordination of strong  $\sigma$  donors such as a peroxo group caused upfield shifts of <sup>95</sup>Mo and <sup>183</sup>W NMR



signals.<sup>[27]</sup> Therefore, the signal at  $\delta = -554.6$  ppm can be assigned to tungsten atoms with the peroxy ligands. The 1:1:1:1 ratio suggests that **II** also has  $C_2$  symmetry. The fully occupied silicododecatungstate,  $[\gamma\text{-SiW}_{12}\text{O}_{40}]^{4-}$ , was completely inactive for the catalytic epoxidation. This fact and the specific regioselectivity for epoxidation of nonconjugated dienes by **I** suggest the formation of an active oxygen species on the divacant lacunary site with the maintenance of  $\gamma$ -Keggin structure.

After the treatment of **I** with 30% hydrogen peroxide followed by the addition of an excess of diethyl ether, a precipitate was formed. The  $^{29}\text{Si}$  and  $^{183}\text{W}$  NMR spectra of the precipitate were the same as those of **II**, showing the successful isolation of **II** (Figures 4b, 5b, and S2). Positive-ion cold-spray ionization mass spectrometry (CSI-MS) of the isolated compound **II** showed the most intense parent ion peaks centered at  $m/z = 3654.8$  with an isotopic distribution (Figures 6 and S3) that agreed with the calculated pattern of  $[(\text{TBA})_5\text{SiW}_{10}\text{O}_{32}(\text{O}_2)_2]^+$ .

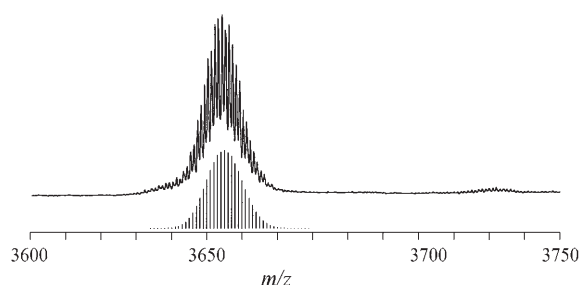


Figure 6. Positive ion CSI-MS ( $m/z$  3600–3750) spectrum of **II** in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (top) and the calculated pattern of  $[(\text{TBA})_5\text{SiW}_{10}\text{O}_{32}(\text{O}_2)_2]^+$  (bottom).

All these results ( $^{29}\text{Si}$  and  $^{183}\text{W}$  NMR spectroscopy, and CSI-MS) show that the two oxo groups ( $\text{O}^{2-}$ ) are replaced by two peroxy species ( $\text{O}_2^{2-}$ ) on the divacant lacunary site with retention of the  $\gamma$ -Keggin framework.<sup>[28]</sup> There are three kinds (**a**, **b**, and **c** in Figure S4) of possible sites for the formation of peroxy groups, taking account of the  $C_2$  symmetry. The strong inhibition of the catalytic reactivity in the presence of coordinative solvents and compounds such as *N,N*-dimethylformamide, dimethyl sulfoxide, pyridine, and imidazole suggests that the coordinatively unsaturated sites of  $[\gamma\text{-SiW}_{10}\text{O}_{34}]^{4-}$ , in which two aquo ligands in **I** are eliminated, play an important role in the activation of hydrogen peroxide. Therefore, **a** would be the most probable site for the formation of the peroxy species.<sup>[29]</sup>

**Reactivity of **II** with olefins:** Under the same reaction conditions as those in Table 1, there was hardly any stoichiometric epoxidation of cyclooctene with the isolated compound **II**, showing that **II** is inactive for the present epoxidation. The induction period was still observed for the epoxidation catalyzed by **II** with hydrogen peroxide (Figure 3). When the formation of **II** was estimated by monitoring the reaction of **I** with excess hydrogen peroxide (20 equiv relative to **I**) by

in-situ IR,  $^{29}\text{Si}$ , and  $^{183}\text{W}$  NMR spectroscopy, and CSI-MS, the formation of **II** was completed within 10 min, a much shorter time than the induction period ( $\approx 60$  min).<sup>[30]</sup> It is therefore probable that the reaction of **II** with hydrogen peroxide leads to formation of a reactive species (**III**) and that the induction period observed in the catalytic epoxidation corresponds to the slow formation of **III** from **II**. Detection of **III** by  $^{29}\text{Si}$  and  $^{183}\text{W}$  NMR spectroscopy was unsuccessful (Figure S5), probably because the quantity of **III** was very small and below the detection limits of  $^{29}\text{Si}$  and  $^{183}\text{W}$  nuclei ( $S/N$  ratio of  $^{29}\text{Si}$  and  $^{183}\text{W}$  NMR spectra = 7–10:1). Similarly, detection of **III** by in-situ IR and Raman spectroscopy was unsuccessful. Epoxidation by molybdenum peroxy complexes was initiated by addition of hydroperoxides, and the proton-transfer reaction from the hydroperoxides to a peroxy ligand was a key step determining the catalytic activity.<sup>[9,14c]</sup> Similarly, hydrogen peroxide would work as a proton donor to form a hydroperoxy species (**III**) such as  $[\text{TBA}]_3[\gamma\text{-SiW}_{10}\text{O}_{32}(\text{O}_2)(\text{OOH})]$  through protonation of **II** in the present system. The induction period almost disappeared with addition of a small amount of  $\text{HClO}_4$  (0.125–0.250 equiv relative to **I**) (Figure 3). In addition, good linear correlation was observed between the reaction rates for epoxidation of cyclooctene in the presence of perchloric acid and additional amounts of perchloric acid (Figure S6). All of these results support the generation of the hydroperoxy species **III**. Such an activation mode and different structure may result in the reactivity of **I** being unusual when compared with that of  $[\text{DTMA}]_2[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]$  and  $[\text{THA}]_3[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]$ .<sup>[6]</sup> In the presence of **II** and hydrogen peroxide (5 equiv relative to **II**), the ratio of less substituted epoxides to total epoxides was 0.87:1 for the epoxidation of 1-methyl-1,4-cyclohexadiene and the  $X_{\text{SO}}$  value was 0.03 for the oxidation of SSO. The good agreement of these values with the respective values of 0.89:1 and 0.04 observed for the catalytic reaction with hydrogen peroxide by **I** shows that **III** is involved in the catalytic cycle.

**$^{18}\text{O}$ -labeling experiments:** The origin of the oxygen atoms incorporated in the epoxides was investigated with  $^{18}\text{O}$ -labeling experiments. The epoxidation of cyclooctene with **II** ( $[\text{TBA}]_4[\gamma\text{-SiW}_{10}\text{O}_{32}(^{16}\text{O}_2)_2]$ ) in the presence of  $\text{H}_2^{18}\text{O}_2$  (4.5 equiv relative to **II**, in  $\text{H}_2^{18}\text{O}$ ) gave 1,2-epoxycyclooctane with an  $^{18}\text{O}$  content of  $70 \pm 3\%$  (Figure 7a). No  $^{18}\text{O}$  atoms were incorporated in the epoxide with  $\text{H}_2^{16}\text{O}_2$  (in  $\text{H}_2^{18}\text{O}$ ) (Figure 7d), showing that all the  $^{18}\text{O}$  atoms incorporated in the epoxide originate from  $\text{H}_2^{18}\text{O}_2$ . The  $^{18}\text{O}$  content in the epoxide, ( $^{18}\text{O}$ -labeled epoxide)/(total epoxide), did not change during the reaction, depended on the amount of  $\text{H}_2^{18}\text{O}_2$  used, and agreed with the  $^{18}\text{O}$  content in the peroxide,  $[\text{H}_2^{18}\text{O}_2]/([\text{H}_2^{18}\text{O}_2] + [\text{W}(^{16}\text{O}_2)])$  in **II** (Figure 7, inset). These facts demonstrate the equilibration between  $\text{H}_2^{18}\text{O}_2$  and  $\text{W}(^{16}\text{O}_2)$  in **II**. CSI-MS of the compound recovered after the reaction of **II** with excess  $\text{H}_2^{18}\text{O}_2$  (60 equiv relative to **II**, in  $\text{H}_2^{18}\text{O}$ ) showed the most intense parent ion peaks of  $[(\text{TBA})_5\text{SiW}_{10}\text{O}_{32}(^{18}\text{O}_2)_2]^+$  centered at  $m/z = (3654.8 + 8.0)$ , whereas the CSI-MS spectrum of the compound recovered

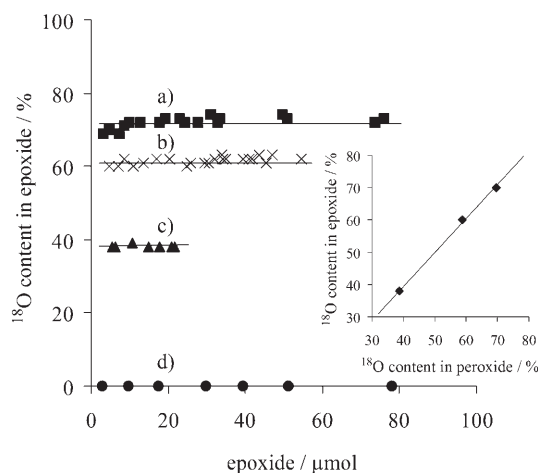
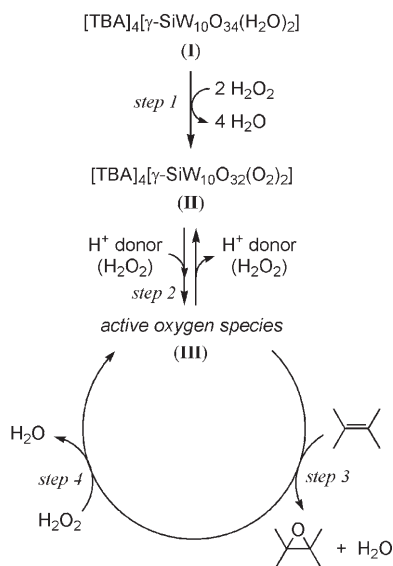


Figure 7. Plots of the ratio of  $^{18}\text{O}$  contents in the epoxide against the amounts of epoxide formed during epoxidation of cyclooctene with 2.2% aqueous hydrogen peroxide. Reaction conditions: **II** (20  $\mu\text{mol}$ ), cyclooctene (1 mmol),  $\text{CH}_3\text{CN}$  (3 mL), 305 K, under 1 atm of Ar. a)  $\text{H}_2^{18}\text{O}_2$  (in  $\text{H}_2^{18}\text{O}$ , 91  $\mu\text{mol}$ ); b)  $\text{H}_2^{18}\text{O}_2$  (in  $\text{H}_2^{18}\text{O}$ , 56  $\mu\text{mol}$ ); c)  $\text{H}_2^{18}\text{O}_2$  (in  $\text{H}_2^{18}\text{O}$ , 25  $\mu\text{mol}$ ); d)  $\text{H}_2^{16}\text{O}_2$  (in  $\text{H}_2^{18}\text{O}$ , 91  $\mu\text{mol}$ ). Inset: Plots of  $^{18}\text{O}$  content in the epoxide against  $^{18}\text{O}$  content in the peroxide. Slope = 1.05 ( $R^2 = 0.99$ ).

after the reaction of **II** with excess  $\text{H}_2^{16}\text{O}_2$  (in  $\text{H}_2^{18}\text{O}$ ) was the same as that of **II** (Figure S7). These facts are in accord with the exchange between  $\text{H}_2^{18}\text{O}_2$  and  $\text{W}^{(16}\text{O}_2)$  in **II**.<sup>[31,32]</sup>

**Mechanism and kinetics:** On the basis of all the results, we propose a reaction mechanism for the epoxidation of olefins with hydrogen peroxide catalyzed by **I** (Scheme 1). First, **I**



Scheme 1.

reacts with hydrogen peroxide to form the diperoxo species **II** (step 1). The reaction of **II** with water did not lead to the formation of **I**, suggesting that step 1 is irreversible. Oxygen transfer from **II** to the C=C bond of the olefin did not occur

under the present conditions and **II** reacts further with hydrogen peroxide to form the active oxygen species **III** (step 2). These steps probably correspond to the induction period observed in the catalytic epoxidation. The oxygen atom of **III** transfers to the C=C double bond, giving the corresponding epoxide (step 3). Finally, **III** is regenerated by reaction with hydrogen peroxide (step 4).

The kinetic data for the present epoxidation were collected after pretreatment of **I** with hydrogen peroxide to make the induction period disappear. Saturation kinetics was observed for the dependence of the reaction rates on the concentration of cyclooctene (0.06–1.15 M, Figure 8a). Kinetic

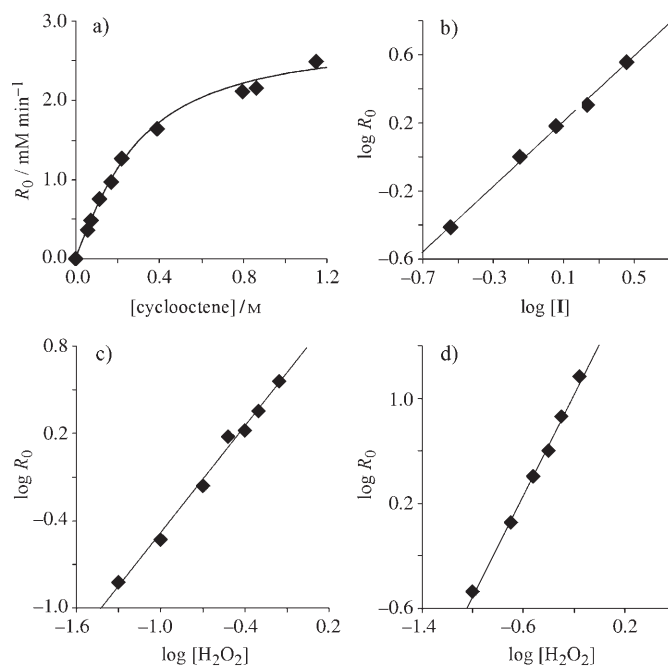


Figure 8. Dependence of reaction rates on the concentrations of a) cyclooctene; b) **I**; c and d) hydrogen peroxide. Conditions: a) cyclooctene (0.06–1.15 M), **I** (1.14 mM),  $\text{H}_2\text{O}_2$  (0.71 M),  $\text{H}_2\text{O}$  (1.67 M),  $\text{CH}_3\text{CN}$  (7 mL), 305 K; b) cyclooctene (0.20 M), **I** (0.29–2.86 mM),  $\text{H}_2\text{O}_2$  (0.30 M),  $\text{H}_2\text{O}$  (1.60 M),  $\text{CH}_3\text{CN}$  (7 mL), 305 K; c) cyclooctene (0.20 M), **I** (1.14 mM),  $\text{H}_2\text{O}_2$  (0.05–0.70 M),  $\text{H}_2\text{O}$  (1.60 M),  $\text{CH}_3\text{CN}$  (7 mL), 305 K; d) cyclooctene (0.95 M), **I** (1.14 mM),  $\text{H}_2\text{O}_2$  (0.10–0.70 M),  $\text{H}_2\text{O}$  (1.60 M),  $\text{CH}_3\text{CN}$  (7 mL), 305 K. The epoxidation was initiated by addition of cyclooctene after pretreatment of **I** with aqueous hydrogen peroxide for 60 min at 305 K, and  $R_0$  values were determined from the reaction profiles at low conversions (<10%) of both cyclooctene and hydrogen peroxide. b) Slope = 0.95 ( $R^2 = 0.99$ ). c) Slope = 1.22 ( $R^2 = 0.99$ ). d) Slope = 1.93 ( $R^2 = 0.99$ ).

studies at a low concentration of cyclooctene (0.20 M; that is, in the region of first-order dependence on the concentration of cyclooctene) showed the first-order dependences of the reaction rates on the concentrations of **I** (0.29–2.86 mM, Figure 8b) and hydrogen peroxide (0.05–0.70 M, Figure 8c), whereas the first- and second-order dependences of the reaction rates on the concentration of **I** (0.29–2.86 mM, Figure S8) and on the concentration of hydrogen peroxide (0.10–0.70 M, Figure 8d), respectively, were observed at a high concentration of cyclooctene (0.95 M, that is, in the

region of zero-order dependence on the concentration of cyclooctene). These dependences can be explained by the change in the rate-determining step from the oxygen transfer to the C=C double bond (at a low concentration of cyclooctene) to the regeneration of **III** (at a high concentration of cyclooctene) (see Kinetic derivations, in the Experimental Section).

## Conclusion

The lacunary polyoxometalate **I** is an effective homogeneous catalyst for the oxygen-transfer reactions of various substrates, including olefins, allylic alcohols, and sulfides, with high efficiency of hydrogen peroxide utilization. The results for the competitive oxidation of *p*-substituted styrenes, oxidation of SSO, and epoxidation of 3-methyl-1-cyclohexene with hydrogen peroxide catalyzed by **I** show that a strongly electrophilic oxidant species with steric hindrance is generated.  $^{29}\text{Si}$  and  $^{183}\text{W}$  NMR spectroscopy and CSI-MS show that the reaction of **I** with hydrogen peroxide leads to generation of the diperoxo species **II**. While the isolated compound **II** is inactive for the stoichiometric epoxidation of cyclooctene, the epoxidation using **II** proceeds in the presence of hydrogen peroxide. The reaction of **II** with hydrogen peroxide forms an active oxygen species **III**, and the induction period observed for the catalytic epoxidation corresponds mainly to the formation of **III**. Kinetic, spectroscopic, and mechanistic investigations show that the **I**-catalyzed olefin epoxidation proceeds via **III**.

## Experimental Section

**Instruments:** IR spectra were measured on a Jasco FT/IR-460 spectrometer Plus using KBr disks. In-situ IR spectra were measured on a Mettler Toledo React IR 4000 spectrometer. NMR spectra were recorded at 298 K on a JEOL JNM-EX-270 spectrometer ( $^1\text{H}$ , 270.0 MHz;  $^{13}\text{C}$ , 67.80 MHz;  $^{29}\text{Si}$ , 53.45 MHz;  $^{183}\text{W}$ , 11.20 MHz). Chemical shifts ( $\delta$ ) were reported downfield from  $\text{SiMe}_4$  (solvent,  $\text{CDCl}_3$ ) for  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra, and from  $\text{Na}_2\text{WO}_4$  (solvent,  $\text{D}_2\text{O}$ ) for  $^{183}\text{W}$  NMR spectra. UV/Vis spectra were recorded on a Perkin Elmer Lambda 12 spectrometer. GC analyses were performed on a Shimadzu GC-14B with a flame ionization detector equipped with a TC-WAX capillary (internal diameter = 0.25 mm, length = 30 m) or a SE-30 packed column. HPLC analyses were performed on Agilent 1100 series LC with a UV/Vis detector using a CAPCELL PAK MG  $\text{C}_{18}$  reverse-phase column (5  $\mu\text{m} \times 3 \text{ mm} \varphi \times 250 \text{ mm}$ , Shiseido Fine Chemicals). Mass spectra were recorded on a Shimadzu GCMS-QP2010 equipped with a DB-WAX capillary column (internal diameter = 0.25 mm, length = 30 m), at an ionization voltage of 70 eV. CSI-MS spectra were recorded on a JMS-T100 LC spectrometer. Typical measurements were as follows: orifice voltage 90 V and  $-95 \text{ V}$  for positive and negative ions, respectively; sample flow 0.05  $\text{mL min}^{-1}$ ; solvent  $\text{ClCH}_2\text{CH}_2\text{Cl}$ ; concentration 0.3 mM; spray temperature 263 K; ion source at room temperature.

**Synthesis and characterization of the tetra(*n*-butyl)ammonium salt of **I**:** The tetra(*n*-butyl)ammonium salt derivative of  $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$  was prepared by cation exchange. The catalytic activity of  $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$  depended on the pH upon preparation of the corresponding tetra(*n*-butyl)ammonium salts, as previously reported.<sup>[6]</sup> Furthermore, it has been reported that  $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$  was changed slowly to  $[\beta_2\text{-SiW}_{12}\text{O}_{40}]^{4-}$  in

strongly acidic aqueous solution ( $\text{pH} < 1$ ),<sup>[33]</sup> so the pH was adjusted during the synthesis of  $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ .  $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}] \cdot 12 \text{H}_2\text{O}$  (6 g, 2 mmol) was dissolved in  $\text{H}_2\text{O}$  (60 mL), and the pH of this aqueous solution was adjusted carefully to 2 with  $\text{HNO}_3$ . The solution was stirred for 15 min at room temperature, then an excess of  $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Br}$  (6.46 g, 20 mmol) was added in a single step. The resulting white precipitate of  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  was collected by filtration and then washed with an excess of  $\text{H}_2\text{O}$ . The crude product was dried, then purified twice by precipitation (addition of  $\text{H}_2\text{O}$  (1 L) to a  $\text{CH}_3\text{CN}$  solution of  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (15 mL)). Analytically pure  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  was obtained as a white powder. Yield 3.4 g (54 %). Data for **I**:  $^{29}\text{Si}$  NMR (53.45 MHz,  $\text{CD}_3\text{CN}/\text{DMSO}$  (2:1 v/v), 298 K):  $\delta$  ( $\Delta\nu_{1/2}$ ) =  $-83.5 \text{ ppm}$  (4.3 Hz);  $^{183}\text{W}$  NMR (11.20 MHz,  $\text{CD}_3\text{CN}/\text{DMSO}$  (2:1 v/v), 298 K):  $\delta$  ( $\Delta\nu_{1/2}$ ) =  $-95.7$  (3.3 Hz),  $-98.9$  (3.3 Hz),  $-118.2$  (4.0 Hz),  $-119.6$  (4.0 Hz),  $-195.7 \text{ ppm}$  (4.3 Hz) with an integrated intensity ratio of 1:1:1:1, respectively; UV/Vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}} = (\epsilon)$  275 nm (22000  $\text{mol}^{-1} \text{ m}^3 \text{ cm}^{-1}$ ); IR (KBr):  $\tilde{\nu} = 999, 958, 920, 902, 877, 784, 745, 691, 565, 544 \text{ cm}^{-1}$ ; Raman:  $\tilde{\nu} = 985, 910, 891, 797, 705, 661, 560, 386, 355 \text{ cm}^{-1}$ ; positive ion MS (CSI, acetone):  $m/z$  3622.8  $[(\text{TBA})_3\text{SiW}_{10}\text{O}_{34}]^+$ ; negative ion MS (CSI, acetone):  $m/z$  3137.7  $[(\text{TBA})_2\text{SiW}_{10}\text{O}_{34}]^-$ ; elemental analysis calcd (%) for  $\text{C}_{64}\text{H}_{150}\text{N}_4\text{O}_{37}\text{SiW}_{10}$  ( $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ ): C 22.09, H 4.19, N 1.64, Si 0.80, W 53.24; found: C 22.38, H 4.40, N 1.63, Si 0.82, W 53.53.

**Oxidation with hydrogen peroxide catalyzed by **I**:** Epoxidation of olefins, nonconjugated dienes, and allylic alcohols and oxidation of sulfides were carried out in a glass vessel (30 mL) containing a magnetic stir bar. Acetonitrile (Kanto Chemical, >99.5 %) was dried and stored over 3A molecular sieves. Substrates were purchased from TCI and Aldrich and used without further purification. Nonconjugated dienes were purified by the standard procedure.<sup>[34]</sup> All products were identified by comparison of GC retention times, mass spectra, and NMR spectra with those of the authentic samples and the quantifications were carried out by calibrated GC analyses and/or  $^1\text{H}$  NMR analyses. Detailed data for the typical oxidation products are given in the Supporting Information. The carbon balance in each experiment was in the range 95–100 %.  $\text{H}_2\text{O}_2$  remaining after the reaction was analyzed by  $\text{Ce}^{3+/4+}$  titration.<sup>[35]</sup> A typical procedure for the catalytic epoxidation of olefins was as follows. The reaction vessel was charged with catalyst containing tungsten (80  $\mu\text{mol}$ ) (that is, **I**, 8  $\mu\text{mol}$ ;  $[\text{THA}]_3[\text{PO}_4[\text{WO}(\text{O}_2)_2]_4]$ , 20  $\mu\text{mol}$ ;  $[\text{DTMA}]_2[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]$ , 40  $\mu\text{mol}$ ); solvent ( $\text{CH}_3\text{CN}$ , 6 mL), substrate (5 mmol), and an internal standard (naphthalene). The reaction was initiated by addition of aqueous  $\text{H}_2\text{O}_2$  (30 %, 1 mmol). The reaction solution was sampled periodically and analyzed by NMR spectroscopy and GC in combination with mass spectrometry.

**Procedure for oxidation of thianthrene 5-oxide (SSO):** The oxidation products were analyzed quantitatively by HPLC: CAPCELL PAK MG  $\text{C}_{18}$  reverse-phase column, 5  $\mu\text{m} \times 3 \text{ mm} \varphi \times 250 \text{ mm}$  (Shiseido Fine Chemicals); eluent,  $\text{CH}_3\text{OH}/\text{CH}_3\text{CN}/\text{H}_2\text{O} = 60:15:25$ ; flow rate 0.4  $\text{mL min}^{-1}$ ; column temperature 30  $^\circ\text{C}$ ; detection at  $\lambda = 254 \text{ nm}$ ; retention times 3.57, 4.69, 4.93, 5.72, 7.73, and 10.7 min for *trans*-thianthrene 5,10-dioxide (SOSO), thianthrene 5,5,10-trioxide (SOSO<sub>2</sub>), *cis*-SOSO, thianthrene 5,5-dioxide (SSO<sub>2</sub>), SSO, and naphthalene (internal standard), respectively. The reaction conditions (for example, concentration of substrate, substrate/oxidant ratio, reaction temperature) were controlled to minimize overoxidation to SOSO<sub>2</sub> and then to estimate the true electronic nature of the oxidant.<sup>[36]</sup> The  $X_{\text{SO}}$  value was calculated according to:<sup>[36]</sup>  $X_{\text{SO}} = (\text{nucleophilic oxidation})/(\text{total oxidation}) = (\text{SSO}_2 + \text{SOSO}_2)/(\text{SSO}_2 + \text{SOSO} + 2\text{SOSO}_2)$ .

**Isolation of diperoxo polyoxometalate **II**:** A solution of the tetra(*n*-butyl)ammonium salt of **I** (0.344 g, 100  $\mu\text{mol}$ ) and aqueous hydrogen peroxide (20 equiv relative to **I**, 30 %, 2 mmol) in acetonitrile (4 mL) was stirred vigorously at 273 K. After 2 h, excess diethyl ether (100 mL) was added to the solution. The resulting precipitate was then filtered off, washed with diethyl ether (20 mL  $\times$  2), and dried in vacuo to afford 0.339 g (99 % yield) of a white powder.  $^{29}\text{Si}$  NMR (53.45 MHz,  $\text{CD}_3\text{CN}$ , 263 K):  $\delta$  ( $\Delta\nu_{1/2}$ ) =  $-83.96 \text{ ppm}$  (0.9 Hz);  $^{183}\text{W}$  NMR (11.20 MHz,  $\text{CD}_3\text{CN}$ , 263 K):  $\delta$  ( $\Delta\nu_{1/2}$ ) =  $-117.3$  (6.5 Hz),  $-125.2$  (5.6 Hz),  $-146.9$  (6.2 Hz),  $-12.5$  (6.6 Hz),  $-548.0 \text{ ppm}$  (12.4 Hz), with an integrated inten-



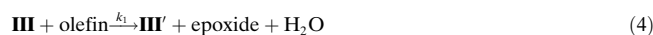
sity ratio of 1:1:1:1:1, respectively; IR (KBr):  $\tilde{\nu}$  = 999, 958, 920, 902, 877, 784, 745, 691, 565, 544  $\text{cm}^{-1}$ ; Raman:  $\tilde{\nu}$  = 911, 886, 841, 801, 779, 748, 692, 649, 553, 539, 524, 510, 384  $\text{cm}^{-1}$ ; positive ion MS (CSI,  $\text{ClCH}_2\text{CH}_2\text{Cl}$ ):  $m/z$  3654.8 [(TBA)<sub>5</sub>SiW<sub>10</sub>O<sub>32</sub>(O<sub>2</sub>)<sub>2</sub><sup>+</sup>]; elemental analysis calcd (%) for C<sub>64</sub>H<sub>144</sub>N<sub>4</sub>O<sub>36</sub>SiW<sub>10</sub> ([[(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>4</sub>[γ-SiW<sub>10</sub>O<sub>32</sub>(O<sub>2</sub>)<sub>2</sub>]): C 22.53, H 4.25, N 1.64, Si 0.82, W 53.88; found: C 21.82, H 4.35, N 1.54, Si 0.80, W 53.05.

**<sup>18</sup>O-labeling experiments:** H<sub>2</sub><sup>18</sup>O<sub>2</sub> (>90% enriched, 2.2% solution in H<sub>2</sub><sup>18</sup>O) was obtained from Isotec. H<sub>2</sub><sup>18</sup>O (97.4% <sup>18</sup>O enriched) was obtained from MSD Isotopes. H<sub>2</sub><sup>16</sup>O<sub>2</sub> (2.2% solution in H<sub>2</sub><sup>18</sup>O) was prepared by dilution of concentrated H<sub>2</sub><sup>16</sup>O<sub>2</sub> (>95%) with H<sub>2</sub><sup>18</sup>O. The ratio of <sup>18</sup>O-labeled epoxide to total epoxide for the epoxidation of cyclooctene with **II** in the presence of H<sub>2</sub><sup>18</sup>O<sub>2</sub> was determined by GC-MS analyses. To recover the product of the reaction of **II** with H<sub>2</sub><sup>18</sup>O<sub>2</sub> (in H<sub>2</sub><sup>18</sup>O), a solution of **II** (4.9 mg, 1.4 μmol) and H<sub>2</sub><sup>18</sup>O<sub>2</sub> (2.2% in H<sub>2</sub><sup>18</sup>O, 60 equiv relative to **II**) in acetonitrile (260 μL) was stirred vigorously at room temperature. After 10 min, the solution was evaporated and dried in vacuo to afford a white powder.

**Kinetic derivations:** The compound **I** reacts with hydrogen peroxide to form the diperoxo species **II** according to Equation (1). The reaction of **II** with water did not lead to the formation of **I**, showing that Equation (2) is irreversible under the present conditions. Compound **II** reacts with H<sup>+</sup> donors such as hydrogen peroxide to form a reactive species **III** according to Equation (3).



The reactions in the catalytic cycle consist of oxygen transfer to olefin from **III** [Eq. (4)], and regeneration of **III** by reaction of **III'** with hydrogen peroxide [Eq. (5)].



The concentration of **III** is expressed by Equation (6). As mentioned under Results and Discussion above, the <sup>29</sup>Si and <sup>183</sup>W NMR spectra of the isolated **II** were intrinsically unchanged by addition of excess hydrogen peroxide, suggesting that the equilibrium constant  $K_1$  is very small. Therefore, the initial concentration of **I** is given by Equation (7).

$$[\mathbf{III}] = K_1 [\mathbf{II}] [\text{H}^+ \text{ donor } (\text{H}_2\text{O}_2)] \quad (6)$$

$$[\mathbf{I}]_{\text{int}} = ([\mathbf{I}] + [\mathbf{III}] + [\mathbf{III}']) \approx [\mathbf{I}] \quad (7)$$

When the oxygen transfer is the rate-determining step, the reaction rate ( $R_0$ ) is expressed by Equation (8), obtained from Equations (4), (6), and (7). When the regeneration is the rate-determining step, the concentration of **III** nearly equals that of **III'** [Eq. (9)], and  $R_0$  is expressed by Equation (10), from Equations (5), (6), and (7).

$$R_0 = k_1 [\mathbf{III}] [\text{olefin}] = k_1 K_1 [\mathbf{I}]^2 [\text{H}^+ \text{ donor } (\text{H}_2\text{O}_2)]^2 [\text{olefin}]^2 \quad (8)$$

$$[\mathbf{III}] \approx [\mathbf{III}'] \ll [\mathbf{I}] \quad (9)$$

$$R_0 = k_2 [\mathbf{III}'] [\text{H}_2\text{O}_2] = k_2 K_1 [\mathbf{I}]^2 [\text{H}^+ \text{ donor } (\text{H}_2\text{O}_2)]^2 [\text{H}_2\text{O}_2] [\text{olefin}]^0 \quad (10)$$

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- [17] The  $\pi(\text{C}=\text{C})$  HOMO energies of 2-methyl-2-pentene, 3-methyl-2-buten-1-ol, and 3-methyl-2-butenyl acetate, calculated at the HF/6-311G(d,p) level, decreased in the order 2-methyl-2-pentene (-8.97 eV) > 3-methyl-2-buten-1-ol (-9.25 eV) > 3-methyl-2-butenyl acetate (-9.71 eV). The electron-withdrawing substituents reduce both the electron density of the C=C double bond and the  $\pi(\text{C}=\text{C})$  HOMO energy, resulting in a decrease in the reactivity of the olefin with electrophilic oxidants. We carried out the competitive epoxidation of 2-methyl-2-pentene, 3-methyl-2-buten-1-ol, and 3-methyl-2-butenyl acetate to confirm the template effect of the present epoxidation. The reactivity decreased in the order 3-methyl-2-buten-1-ol (2.5) > 2-methyl-2-pentene (1.0) > 3-methyl-2-butenyl acetate (0.2). This order is not consistent with that of the  $\pi(\text{C}=\text{C})$  HOMO energies, showing that the template effect reflects the reactivity of these olefins. The template effect was also observed for the epoxidation of geraniol and geranyl acetate.
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- [30] The CSI-MS and in-situ IR spectra measured immediately after addition of hydrogen peroxide (20 equiv relative to **I**) were the same as those of **II**. One <sup>29</sup>Si NMR signal at  $\delta = -84.1$  ppm was observed at 10 min (150 scans) after addition of hydrogen peroxide and the <sup>183</sup>W NMR spectrum of the solution was the same as that of **II** (5000 scans, 60 min). Therefore, we estimated that the formation of **II** was completed within 10 min.
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