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Review

Epoxidation of olefins with hydrogen peroxide catalyzed by polyoxometalates

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Contents

Abstract

Epoxides are an important class of industrial chemicals that have been used as chemical intermediates. Catalytic epoxidation of olefins affords an interesting technology for their production. This review summarizes recent developments for the epoxidation of olefins with hydrogen peroxide catalyzed by polyoxometalates. The versatility, accessibility, and tunability of polyoxometalates open up the development of effective epoxidation systems. Polyoxometalates for H_2O_2-based epoxidation can be classified into two groups according to the structural and mechanistic aspects: (i) catalyst precursors of peroxotungstate or peroxomolybdate species and (ii) oxidatively and hydrolytically stable transition-metal-substituted polyoxometalates.

In addition, we describe our recent studies on the silicotungstate compound, $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$ (**I***), synthesized by protonation of divacant lacunary Keggin-type $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$. The tetra-*n*-butylammonium salt derivative of **I*** (TBA-**I***) exhibits high catalytic activity in the epoxidation of various olefins including non-reactive terminal olefins such as propylene with hydrogen peroxide under mild conditions.
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Keywords: Epoxidation; Olefin; Hydrogen peroxide; Polyoxotungstate

1. Introduction

The epoxidation of olefins is an important reaction in the laboratory as well as in chemical industry [1–3], because epoxides are widely used as raw materials for epoxy resins, paints, surfactants, and are intermediates in organic synthe-

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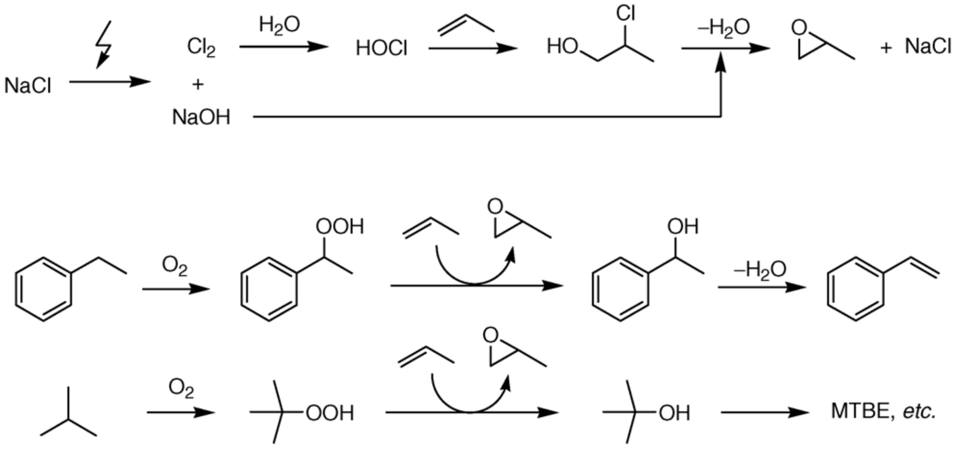
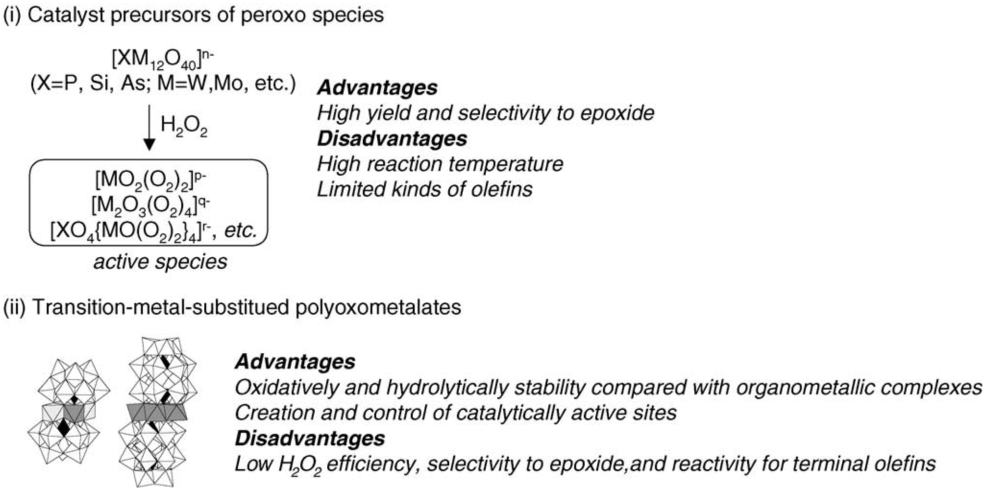


Scheme 1.

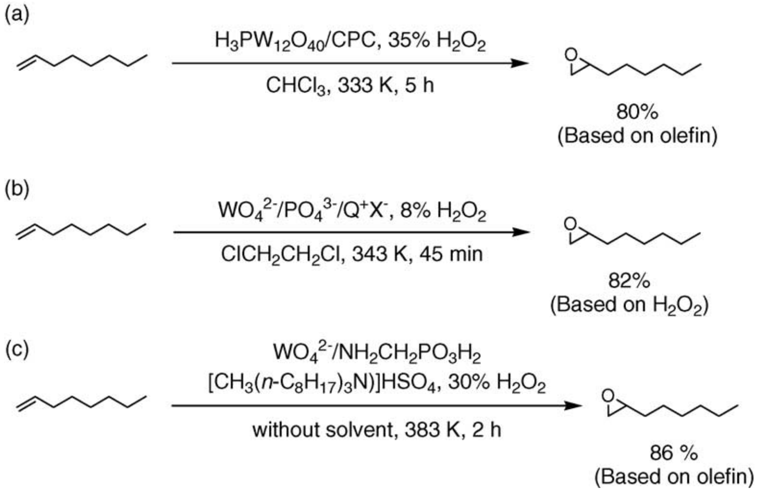
ses. For example, over 5,000,000 and ~70,000 tonnes of propylene and butene oxides, respectively, are produced per year [4]. Although a number of epoxidation processes use various catalysts and oxidants, a chlorine-using non-catalytic process (the chlorohydrin process) and catalytic processes based on organic peroxides and peracids are still used extensively (Scheme 1) [5]. These processes have disadvantages from the economical viewpoint because they are very capital intensive. Furthermore the chlorohydrin process has environmental disadvantages due to the large output of chloride laden sewage. The co-oxidation processes are environmentally acceptable, but the coupling of two products (propylene oxide and styrene or methyl *t*-butyl ether) is commercially undesirable.

In contrast to such classical processes, the catalytic epoxidation with hydrogen peroxide as an oxidant might offer some advantages because (i) it generates only water as a by-product and (ii) it has a high content of active oxygen species [6–9]. Although transition-metal compounds such as metalloporphyrin [10], titanosilicates [11], methyltrioxorhenium [12], tungsten compounds [13–15], polyoxometalates [16,17], manganese complexes [18,19], and non-heme iron complexes [20,21] have been used as effective catalysts for homogeneous and heterogeneous epoxidation with hydrogen peroxide, these systems have some disadvantages. The use of an excess amount of hydrogen peroxide and low pH in an aqueous phase in the case of the biphasic systems lead to the low efficiency of hydrogen peroxide utilization, selectivity to epoxides, especially for the water-soluble shorter-chain epoxides, and stereospecificity [10–21] or the kinds of olefins are limited, e.g., due to the small pore size of TS-1 [22]. In these contexts, effective catalysts for epoxidation of a wide range of olefins with hydrogen peroxide are still desired.

The versatility and accessibility of polyoxometalates have led to various applications in the fields of structural chemistry, analytical chemistry, surface science, medicine, electrochemistry, and photochemistry [23]. Especially, the catalytic function of polyoxometalates has attracted much attention [24–28] because their acidic and redox properties can be controlled at atomic or molecular levels. Various



Scheme 2.



Scheme 3.

catalytic systems for H_2O_2-based epoxidation catalyzed by polyoxometalates have been developed. These systems can be classified into two groups according to the structural and mechanistic aspects of polyoxometalates (Scheme 2).

(i) Catalyst precursors of peroxotungstate or peroxomolybdate species: the monomeric, dimeric, and tetrameric peroxo species are generated by the reaction of polyoxometalates with hydrogen peroxide, and the peroxo species can catalyze the epoxidation. The polyoxometalates act as catalyst precursors.

(ii) Transition-metal-substituted polyoxometalates: transition-metal-substituted polyoxometalates are oxidatively and hydrolytically stable, and various kinds of catalytically active site can be introduced. The sites influence the catalytic activity and selectivity for the epoxidation.

This review focuses on the H_2O_2-based epoxidation of olefins catalyzed by polyoxometalates including our recent investigation on lacunary polyoxometalates, $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$ [29,30]. Recent review articles describe transition-metal-catalyzed epoxidations in more detail [6–9].

2. Epoxidation of olefins with hydrogen peroxide catalyzed by polyoxometalates

2.1. Catalyst precursors of peroxotungstate or peroxomolybdate species

Tungsten-based epoxidation systems with hydrogen peroxide have attracted much attention because of their high reactivities compared with molybdenum analogues and inherent poor activity for decomposition of hydrogen peroxide. Ishii et al. found effective H_2O_2-based epoxidation of terminal olefins catalyzed by $H_3PW_{12}O_{40}$ combined with cetyl pyridinium chloride (CPC) as a phase transfer agent [14] (Scheme 3(a)). Other polyoxometalates such as $H_3PMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_3PMo_6W_6O_{40}$ were much less active than $H_3PW_{12}O_{40}$. Use of biphasic system prevented the hydrolytic cleavage of oxirane rings, resulting in high selectivity to epoxide. This Ishii-system could be applied to the epoxidation of allylic alcohols [14,31], monoterpenes [32], and α,β-unsaturated carboxylic acids [33], oxidation of alcohols [14,31], amines [34], and alkynes [35], and oxidative transformation of diols [14,36–39].

The $[PO_4\{WO(O_2)_2\}_4]^{3-}$ peroxotungstate was isolated and characterized crystallographically by Venturello et al. The anion consisted of the $PO_4{}^{3-}$ anion and two $[W_2O_2(O_2)_4]$ species (Fig. 1). The peroxo species was postulated to be a catalytically active species for the $H_3PW_{12}O_{40}/H_2O_2$ system because $[PO_4\{WO(O_2)_2\}_4]^{3-}$ exhibited a very similar catalytic reactivity to that of the Ishii-system [40]. The spectroscopic and kinetic investigations by Brégeault et al. [41], Griffith and co-workers [42], Thouvenot and co-workers [43], and Hill and co-workers [44] show that the $[PO_4\{WO(O_2)_2\}_4]^{3-}$ is a catalytically important species among various peroxotungstates generated by the reaction of $H_3PW_{12}O_{40}$ with excess hydrogen peroxide (Scheme 4).

H_2O_2-based biphasic epoxidation catalyzed by lanthanide-containing polyoxometalates, $[LnW_{10}O_{36}]^{n-}$ and $[Ln\{PW_{11}O_{39}\}_2]^{m-}$ (Ln = Y, La, Ce, Pr, Sm, Eu, Gd, Dy, Er, Lu, etc.), was reported by Griffith and co-workers [45–50]. Lanthanide plays no roles in the catalysis and indeed in some cases works as an inhibitor. The Raman and

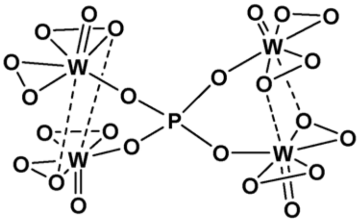
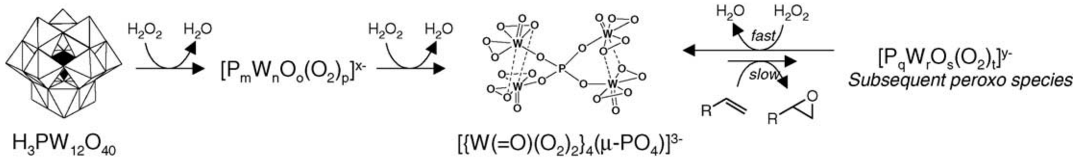


Fig. 1. Molecular structure of $[PO_4\{WO(O_2)_2\}_4]^{3-}$.



Scheme 4.

^{31}P NMR spectroscopy show that peroxotungstates such as $[PO_4\{WO(O_2)_2\}_4]^{3-}$ and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ are active species in the same manner of the Ishii–Venturello system [45–47].

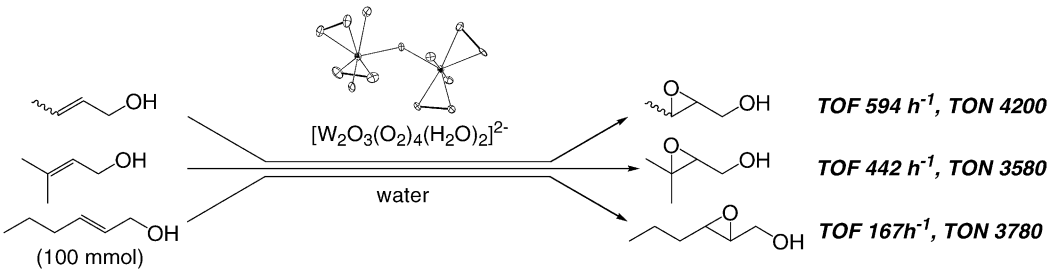
Not only in situ generated peroxo species but also isolated peroxotungstates show a catalytic activity for epoxidation. Various peroxo species have been isolated and characterized crystallographically [40,43,51–63]. Peroxotungstates containing phosphorus or arsenic ligands are generally much more active than $[W_2O_3(O_2)_4]^{2-}$ for the catalytic epoxidation of olefins, especially terminal olefins [42,43,45,52–56,64], while the sulfate species, $[SO_4\{WO(O_2)_2\}_2]^{2-}$, was the most active for the stoichiometric epoxidation of (*R*)-(+)-limonene among $[XO_4\{WO(O_2)_2\}_2]^{2-}$ (X = HAs, HP, and S) peroxotungstates [62,65]. The effects of XO_4 ligands on the reactivity of epoxidation have not yet been clarified. The pH of an aqueous phase and solubility of catalyst to an organic phase have been reported to play an important role in these biphasic epoxidation systems [13–15,41–44]. The structures of peroxo species in aqueous solution depend on the pH, concentration of tungsten and hydrogen peroxide, and molar ratio of hydrogen peroxide to tungsten [66–70]. Very recently, we have shown that the highly chemo-, regio-, and diastereoselective and stereospecific epoxidation of various allylic alcohols with only one equivalent of hydrogen peroxide *in water solvent* could be efficiently catalyzed by an isolated dinuclear peroxotungstate, $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ [71,72] (Scheme 5). A biphasic epoxidation system in the presence of phosphate or arsenate, tungstate, and phase transfer agents (Q^+X^-) under acidic conditions was also reported by Venturello et al. [13] (Scheme 3(b)). Recently, Noyori and co-workers reported an H_2O_2-based epoxidation system without halides and organic solvents using a catalytic system consisting of tungstate, (aminomethyl)phosphonic acid, and methyltrioctylammonium hydrogensulfate [15] (Scheme 3(c)). Although (aminomethyl)phosphonic acid was decomposed into phosphoric acid under the reaction conditions, it facilitated the epoxidation more than phosphoric acid.

Heterogeneous catalysts are more desirable than homogeneous catalysts because they have the following advantages: (i) simple work-up procedures and (ii) the catalysts can be recycled [73]. Immobilization of tungsten compounds on various supports such as anion-exchange resin [74,75], surface-modified silica [76–80], and layered double hydroxide [81–84] have been studied. Jacobs and co-workers reported that $[PO_4(WO(O_2)_2)_4]^{3-}$ supported on a commercial nitrate-form resin was applied to the epoxidation of allylic alcohols and terpenes [74,75]. The catalytic activity of a reused catalyst was completely maintained after several cycles, and the filtrate was catalytically inactive. These results indicate that the observed catalysis is truly heterogeneous in nature.

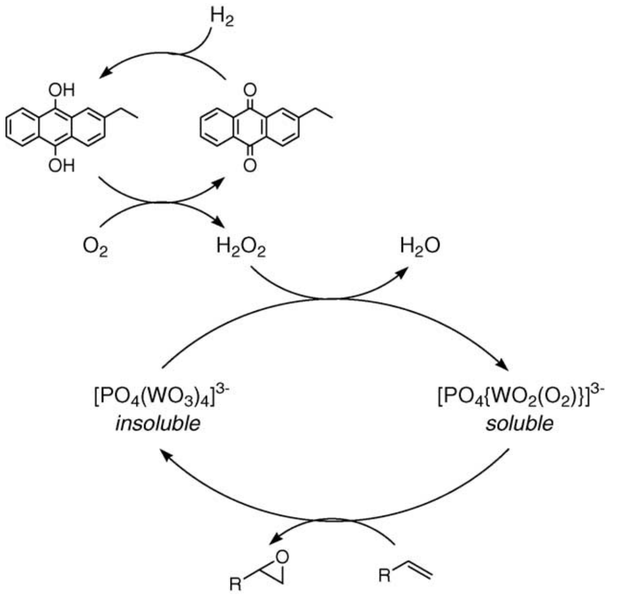
Zuwei et al. developed $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PO_4(WO_3)_4]$-catalyzed epoxidation of olefins in a mixed solvent coupled with the 2-ethylanthraquinone/2-ethylanthrahydroquinone redox process [85]. In this system, initially insoluble $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PO_4(WO_3)_4]$ formed soluble $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PO_4\{WO_2(O_2)\}_4]$ by the reaction with in situ generated hydrogen peroxide. When hydrogen peroxide was completely used, the catalyst became insoluble again. Therefore, the catalyst recovery was simple (Scheme 6).

2.2. Transition-metal-substituted polyoxometalates

Addenda atoms of polyoxometalates can be substituted with various transition metals including chromium, manganese, iron, nickel, cobalt, and noble metals [23–28] (Fig. 2). Transition-metal-substituted polyoxometalates are oxidatively and hydrolytically stable compared with organometallic complexes, and their active sites can be controlled. These advantages have been applied to the development of bio-



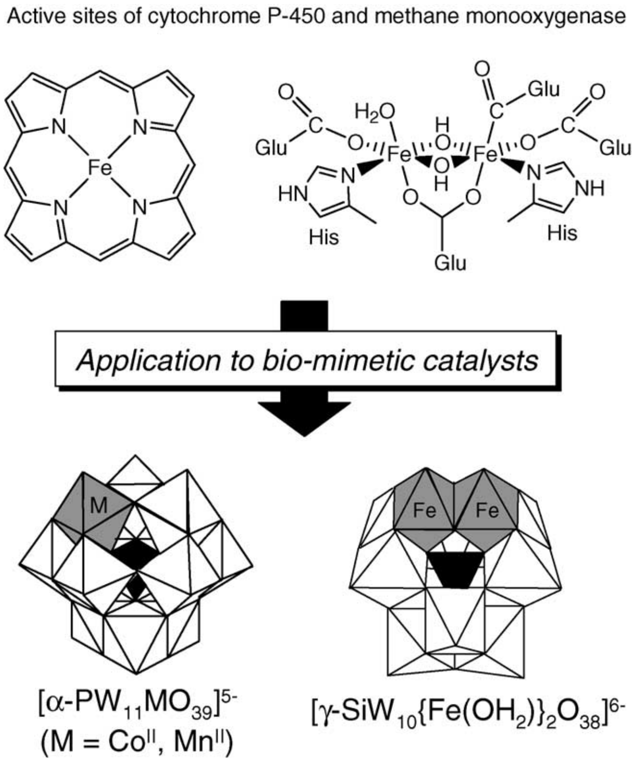
Scheme 5.



Scheme 6.

mimetic catalysts relating to the heme enzyme, cytochrome P-450, and the non-heme enzyme, methane monooxygenase analogues [17,27] (Scheme 7).

Transition-metal-substituted Keggin-type polyoxometalates sometimes promote the decomposition of hydrogen peroxide, allylic oxidation, and hydrolysis of oxirane ring, while Zn, Ti, Fe, and Mn-substituted polyoxometalates can act as effective catalysts for H_2O_2-based epoxidation [44,86-88]. Zinc-containing $[PZn^{II}W_{11}O_{39}]^{5-}$ and $[PZnMo_2W_9O_{39}]^{5-}$ have been reported to be active for the epoxidation although the stability has not been clear [44,89]. Yamase and co-workers proposed that the η^2-peroxo $Ti(O_2)$ species formed by the reaction of $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ with hydrogen peroxide was an active intermediate for epoxidation of olefins [90,91]. Our group synthesized *di*-iron-substituted silicotungstate, $[\gamma\text{-}SiW_{10}\{Fe(OH_2)\}_2O_{38}]^{6-}$, by the reaction of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ with $Fe(NO_3)_3$ in an acidic aqueous solution [92]. This compound could catalyze the selective epoxidation of olefins as well as alkanes with highly efficient utilization of hydrogen peroxide [17,93–95] (Scheme 8). Alkanes could also be oxidized by $[\gamma\text{-}SiW_{10}\{Mn^{III}(OH_2)\}_2O_{38}]^{6-}$ with only 1 atm of molecular oxygen [96].



Scheme 7.

Neumann and co-workers reported that the nickel-substituted quasi-Wells-Dawson-type polyfluorooxometalate,

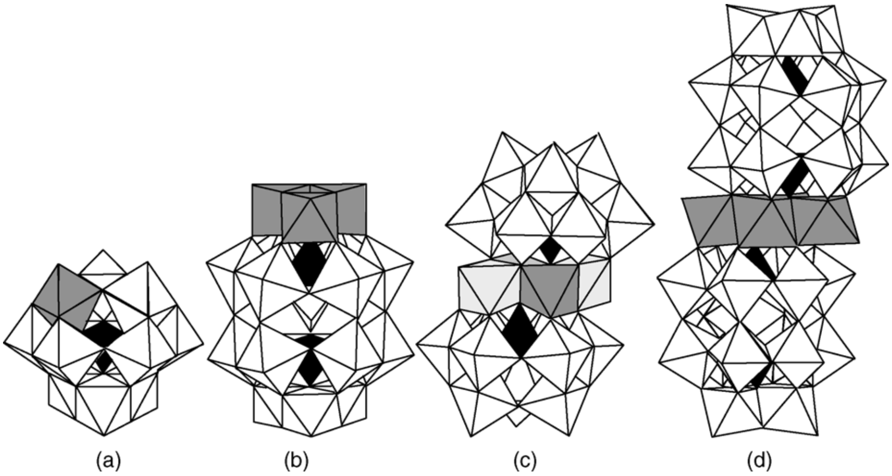
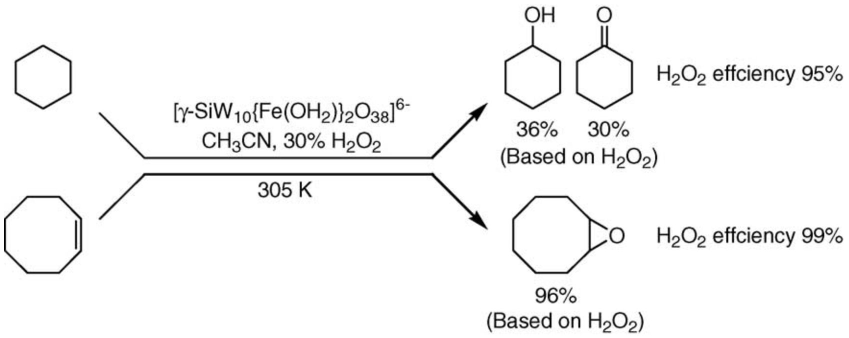


Fig. 2. Polyhedral representations of various transition-metal-substituted polyoxometalates: (a) *mono*-substituted Keggin-type polyoxometalate; (b) *tri*-substituted Wells-Dawson-type polyoxometalate; (c) *tri*-vacant Keggin-type sandwich polyoxometalate; and (d) *tri*-vacant Wells-Dawson-type sandwich polyoxometalate.



Scheme 8.

$[Ni^{II}(H_2O)H_2F_6NaW_{17}O_{55}]^{9-}$, was the most active for epoxidation of olefins and allylic alcohols with hydrogen peroxide among various polyfluorooxometalates [97].

Among the complexes synthesized by the reactions of d-electron transition metals with *tri*-vacant lacunary polyoxometalates, the sandwich-type polyoxometalates have received much attention because of their superior catalytic performance for the oxidation with hydrogen peroxide [16,98–110] and molecular oxygen [111,112]. Furthermore, sandwich-type polyoxometalates have been considered to be more thermodynamically stable than Wells-Dawson and Keggin-type polyoxometalates [16,98,103,113–115]. Neumann and co-workers reported an efficient biphasic H_2O_2-based epoxidation system catalyzed by $[WZnM_2(H_2O)_2(ZnW_9O_{34})_2]^{q-}$ ($M = Mn^{II}$, Zn^{II}, etc.), first synthesized by Tourné et al. [116]. Manganese containing $[WZnMn_2(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ was oxidatively and hydrolytically stable over a range of ≥12,500 turnovers for the epoxidation of cyclooctene [16,98]. Krebs and co-workers synthesized a series of new manganese(II)-substituted polyoxometalates, $[(Mn(H_2O)_3)_2(WO_2)_2(BiW_9O_{33})_2]^{10-}$, $[(Mn(H_2O))_3(SbW_9O_{33})_2]^{12-}$, and $[(Mn(H_2O)_3)_2(Mn(H_2O)_2)_2(TeW_9O_{33})_2]^{8-}$ [104]. These compounds catalyzed regioselective epoxidation of *R*-(+)-limonene to 1,2-epoxide at ambient temperature in a biphasic system. Similarly, epoxidation of *R*-(+)-limonene catalyzed by cobalt-containing sandwich-type polyoxometalate, $[WCo_3(H_2O)_2(CoW_9O_{34})_2]^{10-}$, has been reported while the efficiency of hydrogen peroxide and selectivity to epoxide were very low [106]. Recently, Hill and co-workers synthesized a new family of transition-metal substituted polyoxometalates, $[((MOH_2)M_2PW_9O_{34})_2(PW_6O_{26})]^{17-}$ ($M = Mn^{II}$, Co^{II}), by the decomposition of the sandwich-type polyoxometalates [117]. The methyltricaprylammonium salt of $[((Mn^{II}OH_2)Mn^{II}{}_2PW_9O_{34})_2(PW_6O_{26})]^{17-}$ effectively catalyzed the epoxidation of cyclooctene, cyclohexene, and 1-hexene.

A tetranuclear ferric Wells-Dawson-type sandwich polyoxometalate, $[Fe^{III}{}_4(H_2O)_2(P_2W_{15}O_{56})_2]^{12-}$, showed low selectivity to the corresponding epoxides because of the progress of the allylic oxidation or oxidative cleavage of double bonds similar to Keggin-type analogues [110,114]. In contrast to tetraferric species, a triferric sandwich-type polyoxometalate, $[(NaOH_2)(Fe^{III}OH_2)Fe^{III}{}_2(P_2W_{15}O_{56})_2]^{14-}$, exhibited high selectivity to the corresponding epoxides [118]. A *di*-iron containing sandwich-type polyoxometalate, $[Fe^{III}{}_2(NaOH_2)_2(P_2W_{15}O_{56})_2]^{16-}$, was synthesized using $FeCl_2$ in place of $FeCl_3$ followed by air oxidation in aqueous media, and the Na^+ center could easily be replaced with Cu^{II}, Co^{II}, and Ni^{II} because Na centers were weakly bonded and labile [115,118,119]. Among these compounds, $[Fe^{III}{}_2(NaOH_2)_2(P_2W_{15}O_{56})_2]^{16-}$ and $[Fe^{III}{}_2(NiOH_2)_2(P_2W_{15}O_{56})_2]^{16-}$ exhibited higher activity for the epoxidation of cyclooctene.

While various transition-metal-substituted polyoxometalates can effectively catalyze the epoxidation of olefins with hydrogen peroxide under mild conditions, the efficiency of hydrogen peroxide utilization, selectivity to epoxides, and reactivity for the epoxidation of non-reactive terminal olefins are still low (Table S1) [120,121]. In the next chapter, we describe our recent studies on the epoxidation of olefins catalyzed by lacunary polyoxometalates, $[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$.

2.3. Lacunary polyoxometalate: $[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$

2.3.1. Epoxidation of mono-olefins

In aqueous solution, several polyoxometalate species are present in equilibrium, and the composition depends on pH. Lacunary polyoxometalates are of great importance because they have been used as precursors for various complexes (e.g., transition-metal-substituted polyoxometalates and organic–inorganic hybrid materials).

We are interested in the functionality of lacunary polyoxometalates as a precursor of polynuclear peroxo species because their vacant sites have the possibility to activate hydrogen peroxide catalytically [61]. In contrast to monomeric or dimeric peroxo species, polynuclear peroxo species are expected to show specific reactivity and selectivity because of the electronic and structural characters. A lacunary phosphotungtate, $Na_7PW_{11}O_{39}$, reacted with hydrogen peroxide to form $[PO_4\{WO(O_2)_2\}_4]^{3-}$ [44,122]. On the other hand, silicotungstates are rather stable in water compared with phosphotungstates and the chemistry has been well established by Tézé and Hervé [123].

First, we examined the epoxidation of 1-octene with hydrogen peroxide catalyzed by a series of silicotungstates in acetonitrile at 305 K. The silicotungstates, $[\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$, $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$, $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$, and $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ were converted to the corresponding tetra-*n*-butylammonium salts by the cation exchange reactions. A divacant lacunary silicodecatungstate, $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ (**I**), showed moderate catalytic activity, whereas the other *mono*- and *tri*-vacant lacunary compounds, $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ and $[\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$, as well as a fully occupied silicododecatungstate, $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$, were almost inactive. The catalytic activity of **I** depended on the pH values upon the preparation of the corresponding tetra-*n*-butylammonium salts; the catalyst prepared at pH 2 (compound $\mathbf{I}^*$) exhibited the highest activity: yields after 6 h; **I**; 75% (pH 2) > 52% (pH 1) > 51% (pH 3, 4) > 32% (pH 0). In contrast, effects of proton were hardly observed for the epoxidation reactions catalyzed by $[\text{PO}_4\{\text{WO(O}_2)_2\}_4]^{3-}$ under the present conditions. X-ray crystallographic structural analysis of $\mathbf{I}^*$ was performed on a tetramethylammonium salt derivative, and the formulation of $\mathbf{I}^*$ could be determined as $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$ involving two terminal W–(OH_2) (*aquo* ligand) fragments. Ten tungsten atoms are connected with a central SiO_4 unit, and the structure is classified as γ-Keggin type (Fig. 3). The existence of four $(\text{CH}_3)_4\text{N}^+$ counter cations per $\mathbf{I}^*$ implied that the charge of $\mathbf{I}^*$ was identified to be −4. The bond valence sum values of tungsten (5.90–6.26) and silicon (3.98) indicated that the silicotungstate cluster of $\mathbf{I}^*$ was composed of W(VI) and Si(IV) ions. Therefore, four protons are associated with the anionic cluster of $\mathbf{I}^*$ on the basis of the charge balance. The bond valence sum values of O3 (0.52) and O7 (0.54) were clearly different from those of the other oxygen atoms (1.58–2.11). Moreover, the bond lengths of W2–O3 and W4–O7 (2.16(1) and 2.14(1) Å, respectively) were notably long in comparison with those of other terminal W=O moieties (1.69(1)–1.75(1) Å), and such W–O bond elongation was not observed in the previously reported structure of a non-protonated $\text{K}_8\cdot\mathbf{I}$ [124]. These observations indicate that two oxygen atoms at vacant sites (i.e., O3 and O7) are *di*-protonated resulting in aquo ligands. The ^{183}W NMR spectrum of $\mathbf{I}^*$ showed five resonance lines at −95.2, −98.8, −118.0, −119.1, −195.5 ppm with 1:1:1:1:1 relative intensities, supporting this structure of $\mathbf{I}^*$.

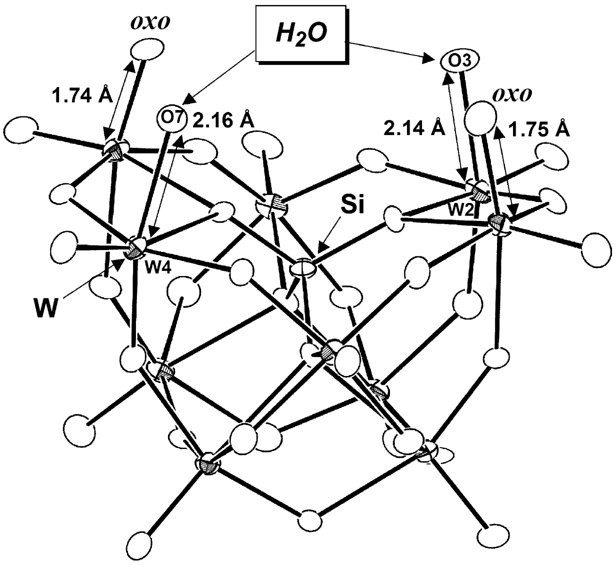


Fig. 3. Molecular structure of $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$.

The catalytic activity of $\mathbf{I}^*$ for the epoxidation of 1-octene was compared with peroxotungstates of $[\text{PO}_4\{\text{WO(O}_2)_2\}_4]^{3-}$ and $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$ on the same loading of tungsten, which have been reported to be effective catalysts for the H_2O_2-based epoxidation [40,42,43,64,71,72]. In each case, the selectivity to 1,2-epoxyoctane was ≥99%, and $\mathbf{I}^*$ showed the highest activity among the catalysts (yield after 10 h; $\mathbf{I}^*$: 90%, $[\text{PO}_4\{\text{WO(O}_2)_2\}_4]^{3-}$: 38%, $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$: 25%).

For the oxygenation of *cis*- and *trans*-2-octenes, the configuration around the C=C moiety was retained in the corresponding epoxides. Moreover, *cis*-2-octene was oxygenated much faster than the *trans* isomer; in the competitive oxygenation of *cis*- and *trans*-2-octenes, the ratio of the formation rate of *cis*-2,3-epoxyoctane to that of *trans* isomer ($=R_{cis}/R_{trans}$) was 11.5. This value is higher than those for the other tungstate–H_2O_2 systems ($H_3PW_{12}O_{40}$: 3.7, $\text{NH}_2\text{CH}_2\text{PO}_3\text{H}_2/\text{WO}_4{}^{2-}$: 7.3 [15]) and for the stoichiometric epoxidation with organic oxidants such as *m*-CPBA (1.2) [125] and dimethyldioxirane (8.3) [126] as shown in Table 1. Such a high stereospecific reactivity of $\mathbf{I}^*$ suggests the contribution of a structurally rigid, non-radical oxidant generated on $\mathbf{I}^*$ (probably at a divacant lacunary site).

The compound $\mathbf{I}^*$ could be applicable to the epoxidation of various olefins (Table 2). Bulky cyclic olefins such as cyclohexene, 1-methyl-1-cyclohexene, cyclooctene, cyclododecene, and 2-norbornene were epoxidized with ≥99% selectivity and ≥99% efficiency of hydrogen peroxide utilization. For some large pore titanium-containing zeolites, epoxides are successively hydrated and the cleavage of oxirane ring framework is caused, resulting in a decrease in the selectivity [127–131]. In the case of the stoichiometric condition (i.e., hydrogen peroxide:cyclooctene = 1:1), the yield of and selectivity to the corresponding epoxide were ≥99%. 1,3-Butadiene was epoxidized selectively to give the corresponding mono-epoxide, without the successive epoxidation of the other C=C fragment (i.e., no di-epoxide was formed). The most notable feature of the catalytic epoxidation with hydrogen peroxide mediated by $\mathbf{I}^*$ was that non-activated terminal C_3–C_8 olefins such as propylene, 1-butene, and 1-octene could be transformed to the corresponding epoxides specifically with ≥99% selectivity and ≥99% efficiency of hydrogen peroxide utilization. Large-scale experiments (100-fold scaled-up) for propylene and 1-octene showed the same results as for the small-scale experiments in Table 2. The decomposition of hydrogen peroxide to form molecular oxygen

Table 1
Comparison of R_{cis}/R_{trans} values for the competitive epoxidation of *cis*- and *trans*-olefins

Entry	System	Olefin	R_{cis}/R_{trans}	Ref.
1[a]	TBA-**I***/H_2O_2	*cis*-2-Octene/*trans*-2-octene	11.5	[29]
2[b]	$H_3PW_{12}O_{40}/H_2O_2$	*cis*-2-Octene/*trans*-2-octene	3.7	[14]
3	$Na_2WO_4{\cdot}2H_2O/NH_2CH_2PO_3H_2/H_2O_2$	*cis*-3-Octene/*trans*-3-octene	7.3	[15]
4	*m*-CPBA	*cis*-2-Octene/*trans*-2-octene	1.2	[125]
5	Dimethyldioxirane	*cis*-3-Hexene/*trans*-3-hexene	8.3	[126]

[a] TBA-**I*** (8 μmol), *cis*-2-octene (5 mmol), *trans*-2-octene (5 mmol), 30% aq. hydrogen peroxide (1 mmol), CH_3CN (6 mL), 305 K.

[b] $H_3PW_{12}O_{40}$ (8 μmol), cetylpyridinium chloride (24 μmol), *cis*-2-octene (1 mmol), *trans*-2-octene (1 mmol), 30% aq. hydrogen peroxide (3 mmol), $CHCl_3$ (5 mL), 333 K.

was negligible, which reduces the risk of building an explosive atmosphere and simplifying the safety measures needed to insure it. Thus, the catalytic performance of **I*** raises the prospect of using this type of catalyst for industrial epoxidation.

The structural stability of **I*** was confirmed by observation of the reaction mixture with an in situ IR spectrometer. No substantial changes of spectral pattern were observed during the catalytic epoxidation by **I*** with hydrogen peroxide. On the other hand, a mixture of $H_3PW_{12}O_{40}$, hydrogen peroxide, and olefin exhibited a drastic change of spectral pattern due to the conversion of $[PW_{12}O_{40}]^{3-}$ to $[PO_4\{WO(O_2)_2\}_4]^{3-}$. The contrast shows that a Si derivative of tetranuclear species (i.e., $[SiO_4\{WO(O_2)_2\}_4]^{4-}$) was not formed in our catalytic system of **I***, hydrogen peroxide, olefin, and acetonitrile. The kinetic study revealed the first-order dependence of the reaction rate on the concentration of **I*** (0.36–3.81 mM), supporting the idea.

The catalyst **I*** could easily be recovered. When the epoxidation of cyclooctene was repeated five times with the recovered catalyst, cyclooctene oxide was quantitatively obtained at the same rate as that for the first run (>99% yield; selectivity to epoxide = 99%). The multinuclear (silicon and tungsten) NMR spectra of the recovered catalyst revealed that the other tungstate compounds such as $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$, $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$, and $[H_nWO_2(O_2)_2]^{(2-n)-}$ were not formed. IR and UV–vis spectra also suggested the maintenance of the γ-Keggin framework of **I*** in the recovered catalyst.

2.3.2. *Epoxidation of non-conjugated dienes*

The intramolecular regioselectivity for the epoxidation of dienes that have two electronically and sterically inequivalent double bonds provides much information about the active species. Generally, more electron-rich double bonds of dienes are preferably epoxidized when stoichiometric oxidants such as peroxyacids [132] and peroxides [133] or hydroperoxides in the presence of molybdenum compounds [134–136] are used. The effects of steric protection of catalysts for the regioselective epoxidation of non-conjugated dienes have been examined. For example, the highly regioselective epoxidation of more accessible, but less nucleophilic double bonds using sterically hindered metalloporphyrins with NaOCl and PhIO have been developed [137–140]. In contrast to these expensive oxidants, hydrogen peroxide is an attractive oxidant from the economical and environmental viewpoints because it generates only water as a by-product and has a high content of active oxygen species. Although various catalysts for the regioselective epoxidation of non-conjugated dienes with hydrogen peroxide have been stud-

Table 2
Epoxidation of various olefins with hydrogen peroxide catalyzed by TBA-**I***[a]

Entry	Substrate	Time (h)	Yield (%)	Product (selectivity (%))	H_2O_2 efficiency (%)
1[b]	Propene	8	90	1,2-Epoxypropane (>99)	>99
2[b]	1-Butene	8	88	1,2-Epoxybutane (99)	>99
3[b]	1,3-Butadiene	9	91	1,2-Epoxy-3-butene (99)	99
4	1-Octene	10	90	1,2-Epoxyoctane (>99)	>99
5	*cis*-2-Octene	3	>99	*cis*-2,3-Epoxyoctane (>99)	>99
6	*trans*-2-Octene	14	91	*trans*-2,3-Epoxyoctane (>99)	99
7	Cyclohexene	6	84	1,2-Epoxycyclohexane (>99)	>99
8	1-Methyl-1-cyclohexne	4	95	1,2-Epoxy-1-methylcyclohexane (>99)	99
9	2-Norbornene	4	>99	*exo*-2,3-Epoxynorbornane (99)	>99
10	Cyclooctene	2	99	1,2-Epoxycyclooctane (>99)	>99
11[c]	Cyclododecene	4	97	1,2-Epoxycyclododecane (>99)	>99

[a] Reaction conditions: TBA-**I*** (8 μmol), olefin (5 mmol), 30% aq. hydrogen peroxide (1 mmol), acetonitrile (6 mL), 305 K. Yield and selectivity were determined by gas chromatography using an internal standard technique. Remaining hydrogen peroxide after reaction was estimated by potential difference titration of Ce^{3+}/Ce^{4+} (0.1 M of aqueous $Ce(NH_4)_4(SO_4)_4{\cdot}2H_2O$). Carbon balance for each reaction was greater than 95%. Yield (%) = products (mol)/H_2O_2 used (mol) × 100. H_2O_2 efficiency (%) = products (mol)/consumed H_2O_2 (mol) × 100.

[b] Propylene (6 atm), 1-butene (3 atm), 1,3-butadiene (2.5 atm).

[c] Acetonitrile (9 mL).

ied [10,32,43,74,75,89,101,104,141–147], the efficiency of hydrogen peroxide utilization and/or the regioselectivity are still low. Therefore, efficient systems for the regioselective epoxidation of dienes with hydrogen peroxide is previously unknown.

Table 3 shows the epoxidation of various dienes with hydrogen peroxide in acetonitrile at 305 K catalyzed by TBA-**I***. Under the present reaction conditions, the amount of di-epoxides and glycols produced through the hydrolysis was negligible in all cases. Under the stoichiometric conditions (1-methyl-1,4-cyclohexadiene (**1a**)/hydrogen peroxide molar ratio = 1:1), the total product yield was 61% and the di-epoxide was formed. Therefore, we used the reaction condition in the high ratio of substrate to hydrogen peroxide. For the epoxidation of **1a** (entry 1), the [**1b**]/[total epoxide] ratio was 0.89 and the more accessible double bond was much more selectively epoxidized. The value was higher than or comparable to those reported for sterically hindered porphyrin systems with NaOCl or PhIO (0.11–0.95) [131,138,140] and the mono-cobalt-substituted heteropolytungstate system with O_2 in the presence of aldehydes (0.69) [148] (Table S2) [149,150]. For the epoxidation of *trans*-1,4-hexadiene (**2a**, entry 2), the terminal double bond was preferably epoxidized. The [**2b**]/[total epoxide] ratio was 0.61 and the value was much higher than those reported for $Mo(CO)_6$/CHP (0.14) [134] and sterically hindered porphyrin systems with NaOCl or PhIO; Mn(TTPPP)(OAc)/NaOCl (0.35) [140], Mn(T(2′,6′-G1APh)P)Cl/PhIO (0.20) [132], Mn(TPP)(OAc)/NaOCl (0.03) [140], and Mn(T(3′,5′-G2Ph)P)Cl/PhIO (0.03) [132] (Table S3).

The epoxidation of *R*-(+)-limonene (**3a**, entry 3) easily proceeded to afford a mixture of diastereoisomeric epoxides and the [**3b**]/[total epoxide] ratio was 0.38. The value was higher than or comparable to those reported for the H_2O_2-based epoxidation; peroxotungstates (<0.03) [32,43,75,144], polyoxometalates (<0.01) [89,104], $Fe(TDCPN_5P)Cl$ (0.27) [141], MTO/UHP (<0.01) [143], manganese complexes (0.17) [74], stoichiometric reactions such as dimethyldioxirane (<0.01) [133], *m*-CPBA (0.09) [132], benzonitrile/$KHCO_3/H_2O_2$ (0.37) [145], and diisopropylcarbodiimide/$KHCO_3/H_2O_2$ (0.18–0.40) [146,147]. Although the regioselectivity for TBA-**I*** is lower than the values reported for sterically hindered porphyrin systems with NaOCl or PhIO (0.62–0.75) [132,140] and various H_2O_2-based systems of Mn(TDCPP)Cl/imidazole (0.59–0.67) [10], $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ (0.50) [101], and Ti-β (0.55) [142], these systems have disadvantages. The use of rather expensive, non-green oxidants such as NaOCl and PhIO, the necessity of excess amounts of oxidant, long reaction time, and high reaction temperature (Table S4) [151,152].

Similarly, the high selectivity to the epoxidation of the electron-poor terminal double bond for the epoxidation of 7-methyl-1,6-octadiene (**4a**, entry 4) was observed. The [**4b**]/[total epoxide] ratio was 0.17 and the value was much higher than those for the H_2O_2-based epoxidation systems of Al_2O_3/H_2O_2 (<0.01) [153], $CF_3CH_2OH/Na_2HPO_4/H_2O_2$ (<0.01) [154], and $(CF_3)_2CO/C_2F_5OH/NaHPO_4/H_2O_2$ (<0.01) [155]. The epoxidation of 4-vinyl-1-cyclohexene (**5a**, entry 5) proceeded exclusively at the ring position rather than the external position, and the [**5b**]/[total epoxide] ratio of 0.04 was lower than those reported for sterically hindered porphyrin systems with NaOCl or PhIO (0.20–0.73) [138,139] and comparable to dendrimer-metalloporphyrins (0.04–0.11) [132]. The results of competitive epoxidation of C_6-olefins which have similar alkyl substituents to the corresponding dienes (**1a**–**5a**) are in good agreement with the trends of regioselectivity for **I*** (Table S5).

The regioselectivity for the epoxidation of various non-conjugated dienes in the present system was compared with those using *m*-CPBA as a stoichiometric oxidant or

Table 3
Epoxidation of various dienes with hydrogen peroxide catalyzed by TBA-**I***[a]

Entry	Diene	Time (h)	Product (yield (%))	***b***/(***b*** + ***c***)	H_2O_2 efficiency (%)
1[b]	1-Methyl-1,4-cyclohexadiene (**1a**)	4	1-Methyl-4,5-epoxy-1-cyclohexene (**1b**, 83) 1-Methyl-1,2-epoxy-4-cyclohexene (**1c**, 10)	0.89	>99
2	*trans*-1,4-Hexadiene (**2a**)	7	1,2-Epoxy-*trans*-4-hexene (**2b**, 43) *trans*-4,5-Epoxy-1-hexene (**2c**, 27)	0.61	81
3[c]	(*R*)-(+)-Limonene (**3a**)	7	8,9-Epoxylimonene (**3b**, 34) 1,2-Epoxylimonene (**3c**, 55)	0.38	93
4	7-Methyl-1,6-octadiene (**4a**)	6	7-Methyl-1,2-epoxy-6-octene (**4a**, 16) 7-Methyl-6,7-epoxy-1-octene (**4b**, 78)	0.17	>99
5	4-Vinyl-1-cyclohexene (**5a**)	4	4-Epoxyethyl-1-cyclohexene (**5a**, 4) 1,2-Epoxy-4-vinylcyclohexane (**5b**, 94)	0.04	98

[a] Reaction conditions: TBA-**I*** (8 μmol), diene (5 mmol), 30% aq. hydrogen peroxide (1 mmol), acetonitrile (6 mL), reaction temperature (305 K). The reaction conditions were controlled to inhibit the double epoxidation. Yields were determined by gas chromatographic analysis with an internal standard technique. Carbon balance for each reaction was greater than 95%. Yield (%) = product (mol)/H_2O_2 used (mol) × 100. Remaining H_2O_2 after the reaction was estimated by potential difference titration of Ce^{3+}/Ce^{4+}. H_2O_2 efficiency = products (mol)/consumed H_2O_2 (mol) × 100.

[b] Toluene was produced as a by-product (7% yield).

[c] Acetonitrile (9 mL).

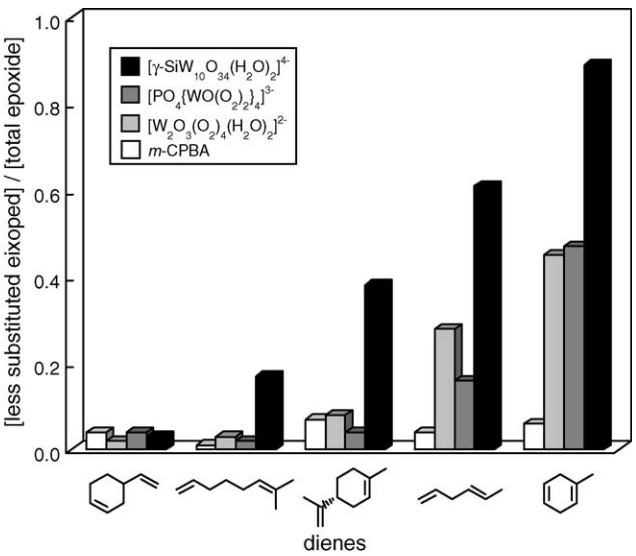


Fig. 4. Ratio of less substituted epoxides to total epoxides formed by the epoxidation of various dienes.

hydrogen peroxide in the presence of peroxotungstates of $[PO_4\{WO(O_2)_2\}_4]^{3-}$ and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$, which have been reported to be effective catalysts for the H_2O_2-based epoxidation [32,43,75,144]. The results are shown in Fig. 4. In the case of *m*-CPBA, more electron-rich double bonds are preferably oxidized in all cases. Among the tungsten catalysts tested, TBA-**I*** showed the highest regioselectivity to the more accessible, but less nucleophilic double bond. In addition, TBA-**I*** showed higher TONs than those for $[PO_4\{WO(O_2)_2\}_4]^{3-}$ and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$. As above mentioned, **I*** was stable under the present reaction conditions. Further, the fact that a fully occupied silicododecatungstate, $[\gamma\text{-}SiW_{12}O_{40}]^{4-}$, was inactive for epoxidation suggests the generation of an active oxidant on a divacant lacunary site.

Table 4 shows the order of reactivity for epoxidation of a series of C_6-olefins catalyzed by **I***. The reactivity was decreased in the order of *cis*-2-hexene (13.9) > 2-methyl-1-pentene (3.1) ~ 2-methyl-2-pentene (3.0) > 2,3-dimethyl-2-butene (2.1) > 1-hexene (1.4) > *trans*-2-hexene (1.0). The π(C=C) HOMO energies of C_6-olefins were calculated at the HF/6-311G(d,p) level and decreased in the order 2,3-dimethyl-2-butene (−8.67 eV) > 2-methyl-2-pentene (−8.97 eV) > *trans*-2-hexene (−9.30 eV) ~ *cis*-2-hexene (−9.32 eV) > 2-methyl-1-pentene (−9.44 eV) > 1-hexene (−9.72 eV). The alkyl substitution increases electron density of the C=C double bond and raises the π(C=C) HOMO energy, resulting in an increase of reactivity of the olefin with electrophilic oxidants without steric hindrance such as peroxyacids, peroxides and peroxo complexes [156–163]. This order is not consistent with that of the π(C=C) HOMO energies of C_6-olefins, but that observed for the epoxidation catalyzed by TS-1, where restricted transition state shape selectivity and diffusion effects were observed [127]. Therefore, the inconsistency of the orders between the π(C=C) HOMO energy and the reactivity would be caused by the steric constraints of the active site of **I***. Further investigation on the epoxidation mechanism is now in progress.

Table 4
Initial and relative rates for the epoxidation of a series of C_6-olefins with hydrogen peroxide catalyzed by TBA-**I***[a]

Entry	Olefin	R_0 (mM min^{-1})	Relative rate[b]
1	*cis*-2-Hexene	3.08	13.9
2	2-Methyl-1-pentene	0.68	3.1
3	2-Methyl-2-pentene	0.68	3.0
4	2,3-Dimethyl-2-butene	0.47	2.1
5	1-Hexene	0.30	1.4
6	*trans*-2-Hexene	0.22	1.0

[a] Reaction conditions: TBA-**I*** (8 μmol), olefin (5 mmol), 30% aq. hydrogen peroxide (1 mmol), acetonitrile (6 mL), reaction temperature (305 K). R_0 values were determined from the reaction profiles at low conversion (≤10%) of hydrogen peroxide.

[b] The values are ratios of R_0/R_0 (*trans*-2-hexene).

3. Conclusion and future opportunities

Polyoxo- and peroxo-tungstates are predominant among simple, soluble metal oxide salts for H_2O_2-based epoxidation, but are sometimes unsuitable for the production of acid-sensitive and/or water-soluble shorter-chain epoxides due to the low pH in an aqueous phase. Although Fe-, Mn-, Co-, Zn-, Ni-substituted polyoxometalates exhibit the high turnover numbers, the efficiency of hydrogen peroxide utilization, selectivity to epoxides, and activity for the epoxidation of non-reactive terminal olefins should be improved. Our recent studies on lacunary polyoxotungstates make it possible that a broad range of olefins are epoxidized under mild conditions with high catalytic activity, selectivity, and efficiency of hydrogen peroxide utilization. The specific reactivity and selectivity caused by the unique structure of lacunary silicotungstate would be applicable to stereo- and shape-selective organic reactions. Heterogeneous catalysts are more desirable than the homogeneous catalysts. To synthesize heterogeneous catalysts based on polyoxometalates for the liquid-phase oxidation, the following items (1) and (2) are important.

(1) Supporting polyoxometalates on an appropriate support without loss of the intrinsic activity and selectivity is interesting.
(2) Complexation of polyoxometalates with appropriate cations to form micro/meso structures would lead to the appearance of shape selectivity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ccr.2004.11.019.

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