Highly Selective, Recyclable Epoxidation of Allylic Alcohols with Hydrogen Peroxide in Water Catalyzed by Dinuclear Peroxotungstate

Keigo Kamata,[a] Kazuya Yamaguchi,[a, b] and Noritaka Mizuno*[a, b]

Abstract: The highly chemo-, regio-, and diastereoselective and stereospecific epoxidation of various allylic alcohols with only one equivalent of hydrogen peroxide in water can be efficiently catalyzed by the dinuclear peroxotungstate, $K_2[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]\cdot 2H_2O$ (**I**). The catalyst is easily recycled while maintaining its catalytic performance. The catalytic reaction mechanism including the exchange of the water ligand to form the tungsten–alcoholate species followed by the insertion of oxygen to the carbon–carbon double bond, and the regeneration of the dinuclear peroxotungstate with hydrogen peroxide is proposed. The reaction rate shows first-order dependence on the concentrations of allylic alcohol and dinuclear peroxotungstate and zero-order dependence on the concentration of hydrogen peroxide. These results, the kinetic data, the comparison of the catalytic rates with those for the stoichiometric reactions, and kinetic isotope effects indicate that the oxygen transfer from a dinuclear peroxotungstate to the double bond is the rate-limiting step for terminal allylic alcohols such as 2-propen-1-ol (**1a**).

Keywords: alcohols · allylic compounds · epoxidation · reaction mechanisms · tungsten

Introduction

Oxidations of organic compounds are important in industry and synthetic chemistry.[1–3] Stoichiometric oxidants such as dichromate, permanganate, and manganese dioxide are often used for the transformations.[1–3] The stoichiometric use and disposal of such oxidants are undesirable from economical and environmental viewpoints. Therefore, much attention has been paid to the use of transition-metal catalysts to achieve the effective oxidation with molecular oxygen and hydrogen peroxide as oxidants.[4–7]

Epoxidation of allylic alcohols is of great importance[8,9] because the epoxides have been used as raw materials for epoxy resins and building blocks for the synthesis of biologically important compounds including natural products,[10,11] and chiral carbons are formed by the epoxidation. Katsuki–Sharpless systems with *tert*-butyl hydroperoxide (TBHP) are an important example for the epoxidation of allylic alcohols while the stereoselective epoxidation needs optically active tartrate.[12] Although many methods for the epoxidation of allylic alcohols have been developed, catalytic processes with expensive and environmentally-unacceptable oxidants such as peracids and hydroperoxides in explosive, hazardous, and carcinogenic organic solvents are still widely used.[13] In this context, the development of efficient catalytic processes by using hydrogen peroxide or molecular oxygen as a green oxidant in non-explosive solvent, especially water, achieve the economical and environmental benefits, and remain challenging.[4–7,14–17]

Many tungsten-based catalysts have been reported to be active for the epoxidation of allylic alcohols with hydrogen peroxide.[18–28] Most of them need strict pH control with amines or buffers and/or use biphasic procedures because of decomposition of both the allylic alcohols and the epoxides.[18–28] We reported very recently an efficient and simple route for epoxidation of both internal and terminal olefins with hydrogen peroxide catalyzed by the divacant lacunary silicotungstate, $[(n\text{-}C_4H_9)_4N]_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$.[29] During the course of our investigation of tungsten-catalyzed oxidation, we found that the simple dinuclear peroxotungstate, $K_2[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]\cdot 2H_2O$ (**I**, Figure 1), could act as an effective catalyst for the epoxidation of allylic alcohols using hydrogen peroxide *in water* under mild reaction conditions [Eq. (1)].[30] To our knowledge, the isolated **I** itself has never been used for the catalytic epoxidation of allylic alcohols using hydrogen peroxide in water without additives al-

[a] K. Kamata, Dr. K. Yamaguchi, Prof. N. Mizuno
Core Research for Evolutional Science and Technology (CREST)
Japan Science and Technology Agency
4-1-8 Honcho, Kawaguchi, Saitama, 332-0012 (Japan)
E-mail: tmizuno@mail.ecc.u-tokyo.ac.jp

[b] Dr. K. Yamaguchi, Prof. N. Mizuno
Department of Applied Chemistry, School of Engineering
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
Fax: (+81) 3-5841-7220

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

DOI: 10.1002/chem.200400352 *Chem. Eur. J.* **2004**, *10*, 4728–4734

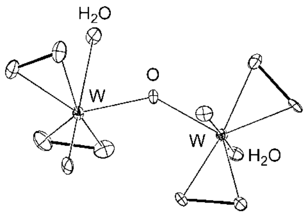
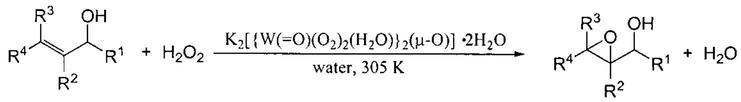


Figure 1. Molecular structure of the anion part of $K_2[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]\cdot 2H_2O$ (**I**).



(1)

though **I** is a previously known compound. In this paper, we report the dinuclear peroxotungstate-catalyzed epoxidation of allylic alcohols with hydrogen peroxide in water, as well as the kinetic and mechanistic aspects of the present epoxidation.

Results and Discussion

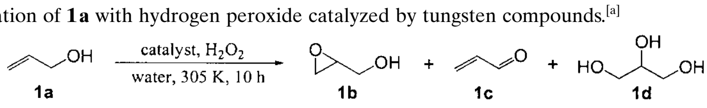
Catalytic epoxidation of allylic alcohols: Epoxidation of **1a** as a model substrate using 30% aqueous hydrogen peroxide in various solvents was carried out in the presence of **I**.[31] Water was the most effective solvent for the present epoxidation: Epoxy alcohol **1b** was formed in a 95% yield with 97% efficiency of hydrogen peroxide utilization under the conditions in Table 1. The use of non-polar toluene, benzene, and dichloromethane solvents (organic/aqueous biphasic system) gave **1b** yields of 90, 80, and 63%, respectively. Water-miscible polar acetonitrile (5% yield) and methanol (<1% yield) were poor solvents probably because of the strong coordination to the tungsten center.[32]

The catalytic activity of **I** for the epoxidation of **1a** was compared with other tungsten compounds such as H_2WO_4 and K_2WO_4 as shown in Table 1. The oxidation did not proceed in the absence of **I** (entry 6). Among tungsten catalysts tested, **I** showed the highest yield of the corresponding epoxide (**1b**): 96% conversion, 99% selectivity to **1b**, and 97% efficiency of hydrogen peroxide utilization for the epoxidation of **1a** (entry 1). The catalyst precursor of K_2WO_4 showed low catalytic activity due to the non-productive decomposition of hydrogen peroxide, and the efficiency of the hydrogen peroxide utilization was low (entry 2). In the case of H_2WO_4, the successive hydrolysis of the product of epoxy alcohol to the corresponding triol **1d** was dominant while the conversion of **1a** was >99% (entry 3). The selectivity to **1b** was increased by the addition of triethylamine to buffer the acidity of the reaction medium (entries 4 and 5).[18,19] However, even in these cases the decomposition of hydrogen peroxide proceeded to some extent due to the basicity of triethylamine.

Table 2 shows the results of epoxidation of various allylic alcohols with 30% aqueous hydrogen peroxide in the presence of **I** without use of the buffer or biphasic system. The pH value of aqueous phase was in the range of 4–5 and no hydrolysis, cleavage, rearrangement of oxirane ring, and allylic oxidation were observed. The catalyst **I** was intrinsically stable in the pH range of 2.5–7 as was confirmed by the ^{183}W NMR and IR spectra. The efficiency of the hydrogen peroxide utilization was more than 90% in each case. Oxidation of simple primary allylic alcohols (**1a**–**5a**) proceeded almost quantitatively and chemoselectively to afford the epoxy alcohols without formation of the corresponding aldehydes and carboxylic acids (entries 1, 2, and 5–7). Larger scale (100 mmol scale) epoxidations of allylic alcohols (**I**:H_2O_2:substrate = 1:5000:5000) showed turnover frequency (TOF) of 594 h^{-1} and turnover number (TON) of 4200 for **2a**, 442 h^{-1} and 3580 for **3a**, and 167 h^{-1} and 3378 for **5a** [Eq. (2)]. These values are higher than those reported to be active for the tungsten-catalyzed epoxidation of internal allylic alcohols with hydrogen peroxide: Na_2WO_4-$NH_2CH_2PO_3H_2$-$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ in toluene, 86 h^{-1} (TOF) and 43 (TON);[24] $[C_5H_5N(n\text{-}C_{16}H_{33})]_3PW_{12}O_{40}$ in 1,2-dichloroethane, 5 h^{-1}, 20;[22] $[(n\text{-}C_4H_9)_4N]_2[PhPO_3\{WO(O_2)_2\}]$ in 1,2-dichloroethane, 80 h^{-1}, 40;[23] $\{WZn[M(H_2O)]_2(ZnW_9O_{34})_2\}^{q-}$ (M: Zn^{2+}, Mn^{2+}, Ru^{3+}, Fe^{3+}, etc.) in 1,2-dichloroethane, 167 h^{-1}, 1000;[27,28] Na_2WO_4-phosphate buffer-β-D-fructopyranoside in water, 0.4 h^{-1}, 10.[26] For the epoxidation of *cis*- and *trans*-allylic alcohols (**2a**, **5a**, and **6a**) the configurations around the C=C moieties were retained in the corresponding epoxy alcohols (entries 2, 7, and 8). Such a stereospecific epoxidation suggests that the free-radical intermediates are not involved in the epoxidation.

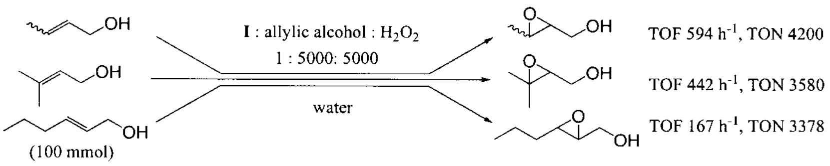
The epoxidation of secondary β,β-disubstituted allylic alcohol (1,3-allylic strained alcohol) of **7a** proceeded diastereoselectively to form mainly the *threo*-epoxy alcohol (entry 9). Allylic alcohols without 1,3-allylic strain (**8a** and **9a**) gave *erythro* rich epoxy alcohols (entries 10

Table 1. Oxidation of **1a** with hydrogen peroxide catalyzed by tungsten compounds.[a]



Entry	Catalyst	Yield [%] 1b	1c	1d	H_2O_2 efficiency [%]
1	$K_2[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]$ (**I**)	95	1	<1	97
2	K_2WO_4	30	<1	<1	32
3	H_2WO_4	<1	<1	>99	>99
4	H_2WO_4/Et_3N (0.29 M)	65	<1	7	76
5	H_2WO_4/Et_3N (0.49 M)	54	<1	1	57
6	no catalyst	no reaction			–

[a] Reaction conditions: **1a** (5 mmol), catalyst (W: 200 μmol, 4 mol%), 30% aq. H_2O_2 (5 mmol), water (6 mL), 305 K. Yields were determined by gas chromatograpy and ^1H NMR with an internal standard technique, and based on **1a**. Residual H_2O_2 after the reaction was estimated by potential difference titration of Ce^{3+}/Ce^{4+} (0.1 M of aqueous $Ce(NH_4)_4(SO_4)_4\cdot 2H_2O)\cdot H_2O_2$ efficiency (%) = products (mol)/consumed H_2O_2 (mol) × 100.



(2)

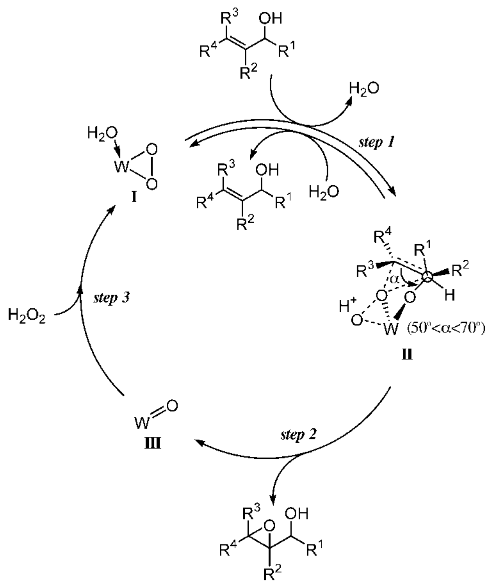
and 12). In addition, epoxidation of allylic alcohol **10a**, in which 1,3- and 1,2-allylic strains compete with each other, was more *erythro* selective (entry 13). 2-Cyclohexen-1-ol gave the corresponding epoxy alcohol (>95% *syn* configuration) in a 40% yield together with a 49% yield of 2-cyclohexen-1-one after 12 h under the same conditions as those in Table 2. It is noted that the epoxidation of 2-cyclohexen-1-ol was highly stereoselective to give the corresponding epoxy alcohol with oxirane ring *cis* to hydroxyl group (*syn* configuration), while large amounts of α,β-unsaturated ketones were produced for the cyclic allylic alcohols. All these results for the epoxidations of secondary allylic alcohols are similar to those for $VO(acac)_2$/TBHP,[9,33–36] $\{WZn[M(H_2O)]_2(ZnW_9O_{34})_2\}^{q-}/H_2O_2$,[27,28] and H_2WO_4/H_2O_2[36] systems in which formation of the metal–alcoholate species in the oxygen transfer step is suggested, and different from those with *m*CPBA,[5,36] dimethyldioxirane,[5,36] and TS-1/urea-hydrogen peroxide[5,36] systems. Further, the regioselective epoxidation of **6a** took place at the electron-deficient allylic 2,3-double bond to afford only 2,3-epoxy alcohol in the high yield (entry 8).

No significant changes in the in situ IR spectra were observed during the catalytic epoxidation of **1a** by **I** with hydrogen peroxide. In addition, the ^{183}W NMR spectrum of the catalyst **I** after the epoxidation of **1a** showed a signal at −704.5 ppm, which was observed for the as-synthesized **I**. IR and UV/Vis spectra of recovered catalyst also suggest the retention of the structure of **I**. These facts show that **I** is stable under the reaction conditions. The first-order dependence of the reaction rate on the concentration of **I** as shown in Figure 3, supports the idea.

The products could easily be isolated by the simple extraction by using dichloromethane or *n*-pentane after the oxidation since catalyst **I** was completely insoluble in these solvents. Actually, no leaching of tungsten into the organic phase was confirmed by inductively coupled plasma atomic emission analysis (ICP-AES). Therefore, the aqueous phase including the catalyst could be recovered without loss of the tungsten species. It is notable that **I** can be reused without loss of the catalytic activity, stereospecificity, and chemo-, regio-, and diastereoselectivity for the epoxidation (entries 3, 4, and 10).

Kinetics and mechanism: The present regioselective epoxidation of allylic alcohol **6a** shows that the allylic hydroxyl function plays an important role in the epoxidation. The need of the hydroxyl functionality is further demonstrated by the complete lack of epoxidation reactivity of the ester and ether derivatives of allyl acetate[37] and 3-methoxy-1-propene. In this epoxidation, it is probable that the allylic hydroxyl groups ligate to the tungsten center to form tungsten–alcoholate bond, which prefers the oxygen transfer to the proximal 2,3-allylic double bond rather than to the remote unfunctionalized 6,7-double bond in the case of **6a**. The analogous formation of metal–alcoholate species is suggested at the oxygen transfer step in the allylic alcohol epoxidation systems of $VO(acac)_2$/TBHP, $Ti(O\textit{i}Pr)_4$/TBHP, $\{WZn[M(H_2O)]_2(ZnW_9O_{34})_2\}^{q-}/H_2O_2$, and H_2WO_4/H_2O_2.[27,28,38] By contrast, non-metal catalyzed *m*CPBA and dimethyldioxirane systems prefer the epoxidation at the 6,7-double bond of **6a**. The selectivity has been explained by the formation of the characteristic hydrogen bonding in the oxygen transfer step.[27,28] In the present **I**-catalyzed system (see above), the epoxidation of 1,3-allylic strained alcohol proceeded diastereoselectively to give the *threo* diastereoisomer preferentially. The *erythro* selectivity was a little higher in the case of the allylic alcohol without 1,3-allylic strain. These facts are similar to those of $VO(acac)_2$/TBHP and H_2WO_4/H_2O_2 (metal–alcoholate binding mechanism), and different from those of *m*CPBA and dimethyldioxirane (hydrogen-bonding mechanism). Further, it is noted that the *threo*/*erythro* ratio in the epoxidation of **10a** catalyzed by **I** (*threo*/*erythro* 34:66) lies between those for $VO(acac)_2$/TBHP (33:67)[28] and $\{WZn[M(H_2O)]_2(ZnW_9O_{34})_2\}^{q-}/H_2O_2$ (45:55).[28] The stereochemical data suggest that the dihedral angle between the π plane of the double bond and the hydroxy group of the allylic alcohol in the transition-state geometry of the oxygen transfer step for **I**-catalyzed epoxidation is 50–70 °C, in accord with the angle reported for the tungsten-catalyzed epoxidation.[28]

On the basis of these results, we propose a possible catalytic cycle for the present epoxidation (Scheme 1). First, the water ligand of peroxotungstate **I** is exchanged by an allylic alcohol to form the tungsten–alcoholate species **II** (step 1). The deprotonation of the O−H bond of an allylic alcohol followed by the proton transfer to the peroxo ligand is included in the step 1. The reaction rate for the epoxidation of **1a** decreased with increase in the concentration of protons (Figure S5), in accord with the presence of step 1 in Scheme 1.[39] Next, the epoxy alcohol and **III** are formed (step 2). Finally, **I** is regenerated by the reaction of **III** with hydrogen peroxide (step 3). The ^{1}H NMR spectrum of the reaction solution of ethanol (870 mM) catalyzed by **I** (50 mM) in D_2O at 305 K after 1 h showed a intense resonance of ethanol together with a set of signals at δ 1.44 (t, $^3J=5.1$ Hz) and δ 2.21 (d, $^3J=2.5$ Hz) due to the methyl protons, at δ 5.35 (q, $^3J=5.1$ Hz) due to the methylene protons, and at δ 9.79 (q, $^3J=2.5$ Hz) due to the formyl proton.[40] The signals at δ 2.21 and 9.79 can be assigned to acetaldehyde. The ^{1}H NMR signals of the α-protons of tungsten–alcoholate species have been reported in the range of δ 4.8–5.8.[41,42] Therefore, the signal at δ 5.35 can be assigned to the methylene protons of the tungsten–ethoxide species formed through the reaction of ethanol with **I**. The signal at δ 1.44 can also be assigned to the methyl protons of the tungsten–ethoxide species. The ^{13}C NMR spectrum showed a resonance at δ 87.9 due to the methylene carbon of the tungsten–ethoxide species.[41,42] These results also suggests the formation of **II** during the present epoxidation.



Scheme 1.

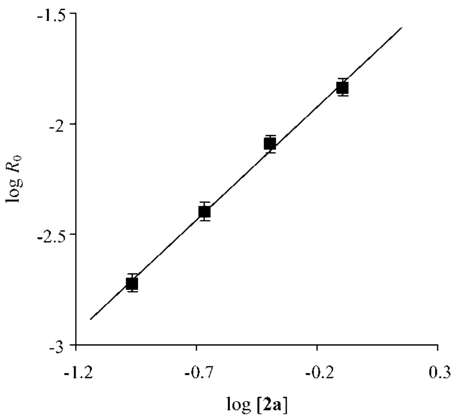


Figure 2. Dependence of reaction rate on concentration of **2a**: **2a** (0.11–0.81 M), **I** (2.22 mM), D_2O/H_2O (0.25/0.75 mL), H_2O_2 (0.56 M), 303 K. R_0 values were determined from the reaction profiles at low conversions (<10%) of both **2a** and hydrogen peroxide. Slope = 1.02.

The kinetic studies for the epoxidation of an internal allylic alcohol **2a** showed the reasonable first-order plots for the loss of concentration of **2a** (0.11–0.81 M) (Figure 2). In addition, the first-order dependences of the reaction rate on the concentration of catalyst **I** (0.92–4.12 mM) (Figure 3) and the zero-order dependence on the concentration of hydrogen peroxide (0.34–0.78 M) (Figure 4) were observed. Kinetic studies on the epoxidation of a terminal allylic alcohol of **1a** also show the first-order dependence of the reaction rate on both concentrations of **1a** (0.31–0.69 M) and catalyst **I** (3.8–11.4 mM), and the zero-order dependence on the concentration of hydrogen peroxide (0.14–0.56 M). Therefore, the reaction rate equation was expressed by following equation [Eq. (3)]. R_0 and k are reaction rate and rate constant, respectively. This means that the transition state is composed of one molecule of **I** and one of an allylic alcohol, but not of hydrogen peroxide.

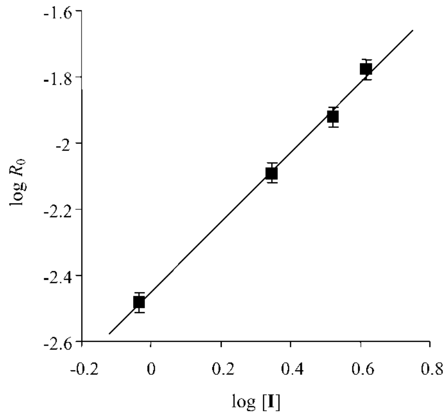


Figure 3. Dependence of reaction rate on concentration of **I**: **2a** (0.40 M), **I** (0.92–4.12 mM), D_2O/H_2O (0.25/0.75 mL), H_2O_2 (0.56 M), 303 K. R_0 values were determined from the reaction profiles at low conversions (<10%) of both **2a** and hydrogen peroxide. Slope = 1.03.

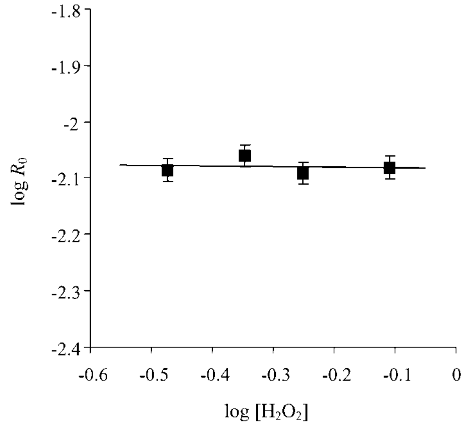


Figure 4. Dependence of reaction rate on concentration of hydrogen peroxide: **2a** (0.40 M), **I** (2.22 mM), D_2O/H_2O (0.25/0.75 mL), H_2O_2 (0.34–0.78 M), 303 K. R_0 values were determined from the reaction profiles at low conversions (< 10%) of both **2a** and hydrogen peroxide. Slope = −0.01.

$$\begin{aligned} R_0 &= -\frac{\mathrm{d}\,[\text{allylic alcohol}]}{\mathrm{d}t} \\ &= k\,[\text{catalyst}\,\mathbf{I}]^1\,[\text{allylic alcohol}]^1\,[\mathrm{H_2O_2}]^0 \end{aligned} \tag{3}$$

The dependence of the reaction rate of **2a** on the temperature (Arrhenius plots, 296–328 K) is shown in Figure 5. The good linearity of the Arrhenius plots was observed to afford the following activation parameters: $E_a = 55.9\ \mathrm{kJ\,mol^{-1}}$, $\ln A = 18.1$, $\Delta H^{\ddagger}_{305\,K} = 53.4\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\ddagger}_{305\,K} = -137.4\ \mathrm{J\,mol^{-1}\,K^{-1}}$, and $\Delta G^{\ddagger}_{305\,K} = 95.3\ \mathrm{kJ\,mol^{-1}}$. The dependence of the reaction rate of **1a** on the temperature was also examined to give the following activation parameters: $E_a = 68.1\ \mathrm{kJ\,mol^{-1}}$, $\ln A = 20.5$, $\Delta H^{\ddagger}_{305\,K} = 65.6\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\ddagger}_{305\,K} = -117.1\ \mathrm{J\,mol^{-1}\,K^{-1}}$, and $\Delta G^{\ddagger}_{305\,K} = 101.3\ \mathrm{kJ\,mol^{-1}}$. The parameters for **2a** was different from those for **1a** while the activation energies (E_a) are in the range of 49–86 $\mathrm{kJ\,mol^{-1}}$ reported for tungsten-catalyzed epoxidation.[43,44]

When the regeneration rate (step 3) was estimated by tracing the reaction of **III** with hydrogen peroxide by using

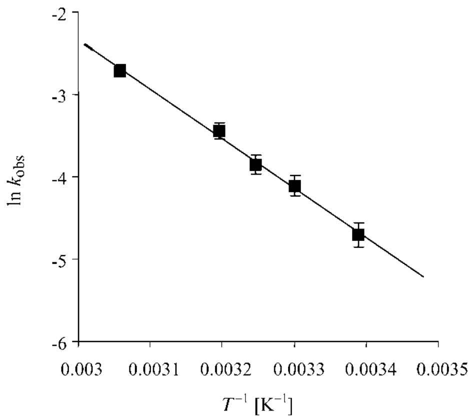


Figure 5. Arrhenius plots for the epoxidation of **2a**: **2a** (0.40 M), **I** (2.22 mM), D_2O/H_2O (0.25/0.75 mL), H_2O_2 (0.56 M), 295–328 K. The observed rate constants (k_{obs}) were calculated with the initial rates by using Equation (3).

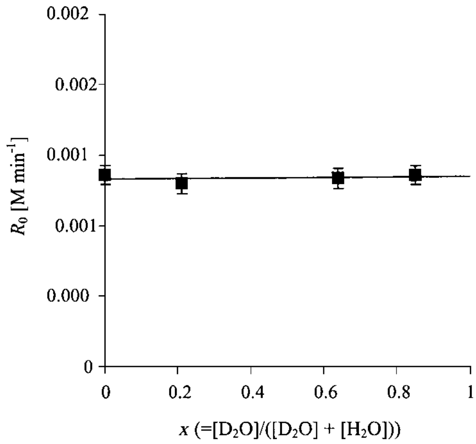
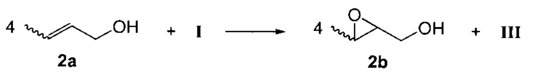


Figure 6. Dependence of epoxidation rate of **1a** on the content of D_2O ($x = [D_2O]/([D_2O] + [H_2O])$): **1a** (0.46 M), **I** (11.1 mM), $D_2O + H_2O$ (1 mL), H_2O_2 (0.56 M), 303 K. R_0 values were determined from the reaction profiles at low conversions (< 10%) of both **1a** and hydrogen peroxide.

an in situ IR spectrometer, the regeneration was completed within 1 min and the rate was larger than that for the catalytic epoxidation reaction under the same conditions. The zero-order dependence on the concentration of hydrogen peroxide was observed. These results show that the regeneration of tungsten species **III** with hydrogen peroxide (step 3) smoothly proceeds and is not a rate-limiting step.

The stoichiometric epoxidation of **2a** (1.9 mmol, 0.40 M) with **I** (40 µmol) produced 166 µmol of **2b**, showing that **I** has 4 equiv active oxygen [Eq. (4)]. The rate of stoichiometric epoxidation of **2a** was 8.1×10^{-3} M min^{-1} and fairly agreed with that of the catalytic epoxidation under the same conditions (8.8×10^{-3} M min^{-1}); this shows that step 3 is not a rate-limiting step.



(4)

Figure 6 shows the dependence of the epoxidation rate of **1a** on the content of D_2O ($x = [D_2O]/([D_2O] + [H_2O])$). The reaction rate was not affected by the presence of D_2O and the proton of the OH group in **1a** was isotopically in equilibrium with the proton in water. These facts show that the deprotonation of O–H bond of an allylic alcohol followed by the protonation of the peroxo ligand is fast and in equilibrium and that the oxygen transfer step from peroxotungstate to an allylic double bond (step 2) is included in a rate-limiting step in the case of a terminal allylic alcohol. On the other hand, the rate for the epoxidation of an internal allylic alcohol **2a** decreased with increasing the contents of D_2O (Figure S6). The decrease in the rate by the presence of D_2O is probably explained as follows: The rate for the **2a** epoxidation was 30 times larger than that for **1a** and therefore the forward process in step 1 would become contributive to a rate-limiting step. The idea is supported by the different activation parameters between **1a** and **2a**.

Conclusion

In summary, the dinuclear peroxotungstate **I** is found to be an effective homogeneous catalyst for the epoxidation of allylic alcohols in water with high efficiency of hydrogen peroxide utilization. Further, **I** can be reused with retention of the high catalytic activity, stereospecificity and chemo-, regio-, and diastereoselectivity for the epoxidation. The kinetic, spectroscopic, and mechanistic investigation show that the dinuclear peroxotungstate-catalyzed allylic alcohol epoxidation proceeds via the O–H bond deprotonation of allylic alcohols followed by the proton transfer to peroxotungstate/alcoholate formation mechanism.

Experimental Section

Instrumentation: GC analyses were performed on Shimadzu GC-14B with a ionization detector equipped with a TC-WAX capillary column. Mass spectra were determined on Shimadzu GCMS-QP2010 at an ionization voltage of 70 eV. NMR spectra were recorded on JEOL JNM-EX-270. ^{1}H and ^{13}C NMR spectra were measured at 270 and 67.5 MHz, respectively, in $CDCl_3$ or D_2O with TMS as an internal or external standard. ^{183}W NMR spectra of **I** were measured at 11.2 MHz in D_2O with Na_2WO_4 (2 M D_2O solution) as an external standard. UV/Vis spectra were recorded on a Perkin–Elmer Lambda 12 spectrometer. IR spectra were measured on Jasco FT/IR-460 Plus using KBr (400–4000 cm^{-1}) or polyethylene disks (below 400 cm^{-1}). In situ IR spectra were measured on a Mettler Toledo React IR 4000 spectrometer.

Materials: Compound **I** was synthesized according to the procedure in ref. [45] and characterized by elemental analysis, IR, UV/Vis, and ^{183}W NMR spectroscopy, and X-ray crystallographic structural analysis. The characterization results are as follows: elemental analysis calcd (%) for $K_2[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]\cdot2H_2O$: H 1.16, O 34.6, K 11.27, W 52.99; found: H 1.12, K 11.98, W 53.19; IR (400–4000 cm^{-1}: KBr disk; below 400 cm^{-1}: polyethylene disk): $\tilde{\nu}$ = 966 $\tilde{\nu}$(W=O), 854 $\tilde{\nu}$(O-O), 764 $\tilde{\nu}_{asym}$(W-O-W), 615 $\tilde{\nu}_{sym}$(W(O$_2$)), 566 $\tilde{\nu}_{asym}$(W(O$_2$), 332 cm^{-1} $\tilde{\nu}$(W(OH$_2$)); UV/Vis (H_2O): λ (ε) = 243 nm (608 M^{-1}cm^{-1}); ^{183}W NMR (11.2 MHz, D_2O, Na_2WO_4, 0.3 M, pH 2.5): δ = −704.5.

Molecular structure of the anion part of **I** is depicted in Figure 1. The method[45] for the preparation of the tetrahexylammonium derivative of $[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$ was modified (i.e., $[(C_6H_{13})_4N]^+$ replaced by [$(n\text{-}C_{12}H_{25})(CH_3)_3N]^+$) for the synthesis of dodecyltrimethylammonium derivative of **I**. The desired dodecyltrimethylammonium derivative was obtained with a 50% yield. Elemental analysis calcd (%) for $[(n\text{-}C_{12}H_{25})(CH_3)_3N]_2[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]$: C 34.35, H 7.00, N 2.70, W 35.48; found: C 35.53, H 6.92, N 2.66, W 35.43; IR (KBr): $\tilde{\nu}$ = 963, 936, 911, 838, 770, 720, 603, 569, 531 cm^{-1}.

Allylic alcohols **7a**, **9a**, and **10a** were synthesized and confirmed by GC analysis in combination with mass and ^1H and ^{13}C NMR spectroscopy as reported previously.[46–49] All epoxy alcohols are known and have been identified by comparison of their ^1H and ^{13}C NMR signals with the literature data.[50–57]

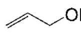
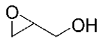
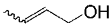
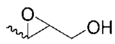
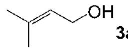
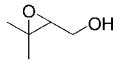
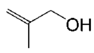
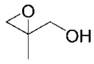
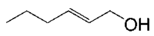
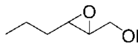
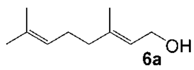
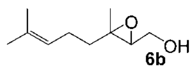
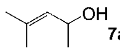
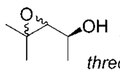
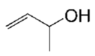
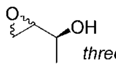
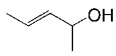
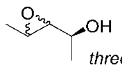
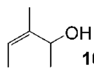
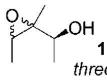
Oxidation of allylic alcohols: The epoxidation was carried out in a glass vial containing a magnetic stir bar. A typical procedure for the epoxidation of allylic alcohol is as follows: Into a glass vial were successively placed **I** (20 μmol), **2a** (5 mmol), hydrogen peroxide (30% aqueous solution, 5 mmol), and water (6 mL). The reaction mixture was stirred at 305 K for 2 h. After the reaction was finished, the products were extracted by using dichloromethane or *n*-pentane, and the yield and product selectivity were determined by GC or ^1H NMR analysis. Recovered aqueous phase was allowed to recycling. Reaction systems are homogeneous except for high-molecular weight alcohol **6a** (entry 8 in Table 2). When the epoxidation of **6a** was carried out with **I** under the conditions in Table 2, only a 20% yield of **6b** was obtained for 10 h. The epoxidation of **6a** efficiently proceeded by using a lipophilic salt, $[(n\text{-}C_{12}H_{25})(CH_3)_3N]_2[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]$, as a catalyst instead of **I**. Large-scale reactions (100 mmol scale) were performed via the same procedures as those above described. The turnover frequencies (TOFs) were determined for the initial stage of the epoxidation (~1 h). Reaction conditions for the larger scale reactions were as follows: Allylic alcohol (100 mmol), **I** (20 μmol), 30% aq. H_2O_2 (100 mmol), water (120 mL), 305 K, 24 h.

Kinetic studies: A NMR tube (5 mm diameter) was used as a reactor for the kinetic studies (spin rate, 15 Hz). It was confirmed that the reaction rates were not affected by the spin rates from 10 to 20 Hz. The reaction was periodically monitored by the ^1H NMR spectra. Reaction conditions are given in the Figure captions (Figure 2–5). Reaction rates (R_0) for the kinetic studies were determined from the slopes of reaction profiles ($[substrate]_0-[substrate]_t$ vs time) at low conversions (< 10%) of the substrate and hydrogen peroxide (initial rate method). Reaction profiles and the first-order plots ($-\ln([substrate]_t/[substrate]_0$ vs time) were shown in Figure S1–S4, Supporting Information. The rate constants determined by the slopes were in good agreement with those determined by the initial rate method.

Stability of catalyst I: The in situ IR spectra of the reaction solution (**1a** (2.0 M), **I** (0.1 M), H_2O_2 (2.0 M), water (10 mL), 298 K) were measured with an in situ IR spectrometer to confirm the structure stability of **I**. The band positions and intensities characteristic of **I**, that is, $\tilde{\nu}$(W=O) (966) and $\tilde{\nu}$(O-O) (854 cm^{-1}), were periodically monitored. The $\tilde{\nu}$(W-O-W) band could not be observed because of overlap with the intense background of water absorption. No substantial changes in the IR spectra were observed during the catalytic epoxidation. More concentrated solution (**1a** (2.0 M), **I** (0.3 M), H_2O_2 (2.0 M), D_2O (3 mL)) was used for the ^{183}W NMR measurement because of the lower sensitivity. Under the conditions, the epoxidation of **1a** was completely finished for 20 min. The ^{183}W NMR spectrum showed a signal at −704.5 ppm for the acquisition during catalysis (500 scans, 20 min).

After the epoxidation was completed (reaction conditions in Table 1), the products were separated by the extraction with dichloromethane or *n*-pentane and the volume of the aqueous phase was reduced to the half by the evaporation. To the solution, ethanol (20 mL) was added and the precipitate was recovered by the filtration. The stability of the recovered **I** was confirmed by the IR (KBr disks) and UV/Vis spectra (0.1 mM in H_2O).

Table 2. Epoxidation of various allylic alcohols with hydrogen peroxide in water catalyzed by **I**.[a]

Entry	Substrate	t [h^{-1}]	Product	Yield [%]
1[b]	 **1a**	10	 **1b**	95
2[c]	 **2a**	2	 **2b**	96
3[c,d]	reuse 1	2		97
4[c,d]	reuse 2	2		97
5	 **3a**	2	 **3b**	97
6	 **4a**	4	 **4b**	90
7	 **5a**	5	 **5b**	98[e]
8[f]	 **6a**	12	 **6b**	85[e]
9	 **7a**	6	 **7b** *threo*/*erythro* 94:6	85
10[b]	 **8a**	10	 **8b** *threo*/*erythro* 24:76	83[g]
11[b,d]	reuse 1	10		89[h]
12	 **9a**	4	 **9b** *threo*/*erythro* 38:62	83[i]
13	 **10a**	5	 **10b** *threo*/*erythro* 34:66	77

[a] Reaction conditions: Allylic alcohol (5 mmol), **I** (20 μmol, 0.4 mol%), 30% aq. H_2O_2 (5 mmol), water (6 mL), 305 K. Yields were based on allylic alcohol which were determined by GC and ^1H NMR using an internal standard technique. [b] **I** (100 μmol, 2 mol%). [c] Substrate: *cis*/*trans* 13:87, epoxy alcohol: *cis*/*trans* = 13:87. [d] Reuse experiment. [e] Isolated yield. [f] $[(n\text{-}C_{12}H_{25})(CH_3)_3N]_2[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]$ (20 μmol) was used as a catalyst. [g] 3-Buten-2-one was produced as a by-product (7% yield). [h] 3-Buten-2-one was formed as a by-product (9% yield). [i] 3-Penten-2-one was formed as a by-product (9% yield).

Acknowledgement

This work was supported in part by the Core Research for Evolutional Science and Technology (CREST) program of Japan Science and Technology Corporation (JST) and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

[1] R. A. Sheldon, J. K. Kochi, *Metal Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, **1981**.
[2] C. L. Hill in *Advances in Oxygenated Processes*, *Vol. 1* (Eds.: A. L. Baumstark), JAI Press, London, **1988**, pp. 1–30.
[3] M. Hudlucky, *Oxidations in Organic Chemistry*, ACS Monograph Series, American Chemical Society, Washington, DC, **1990**.
[4] P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, **1998**.
[5] J. H. Clark, *Green Chem.* **1999**, *1*, 1.
[6] R. A. Sheldon, *Green Chem.* **2000**, *2*, G1.
[7] P. T. Anastas, L. B. Bartlett, M. M. Kirchhoff, T. C. Williamson, *Catal. Today* **2000**, *55*, 11.
[8] K. A. Jørgensen, *Chem. Rev.* **1989**, *89*, 431.
[9] W. Adam, T. Wirth, *Acc. Chem. Res.* **1999**, *32*, 703.
[10] P. A. Bartlett, *Tetrahedron* **1980**, *36*, 2.

[11] P. Besse, H. Veschambre, *Tetrahedron* **1994**, *50*, 8885.
[12] T. Katsuki, K. B. Sharpless, *J. Am. Chem. Soc.* **1980**, *102*, 5974.
[13] A. S. Rao, *Comprehensive Organic Synthesis*, *Vol. 7* (Eds.: B. M. Trost), Pergamon Press, Oxford, **1991**, pp. 357–387.
[14] G.-J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636.
[15] Thematic issue on "Green Chemistry": *Acc. Chem. Res.* **2002**, *35*, 685.
[16] Thematic issue on "Organic Reaction in Water": *Adv. Synth. Catal.* **2002**, *3–4*, 219.
[17] R. Noyori, M. Aoki, K. Sato, *Chem. Commun.* **2003**, 1977.
[18] Z. Racizsewski, *J. Am. Chem. Soc.* **1960**, *82*, 1267.
[19] D. Prat, B. Delpech, R. Lett, *Tetrahedron Lett.* **1986**, *27*, 711.
[20] J. Prandi, H. B. Kagan, H. Mimoun, *Tetrahedron Lett.* **1986**, *27*, 2617.
[21] M. Quenard, V. Bonmarin, G. Gelbard, *Tetrahedron Lett.* **1987**, *28*, 2237.
[22] Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida, M. Ogawa, *J. Org. Chem.* **1988**, *53*, 3587.
[23] G. Gelbard, F. Raison, E. R. Lachter, R. Thouvenot, L. Ouahab, D. Grandjean, *J. Mol. Catal. A* **1996**, *114*, 77.
[24] K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, R. Noyori, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 905.
[25] D. Hoegaerts, B. F. Sels, D. E. de Vos, F. Verpoort, P. A. Jacobs, *Catal. Today* **2000**, *60*, 209.
[26] C. Denis, K. Misbahi, A. Kerbal, V. Ferrieres, D. Plusquellec, *Chem. Commun.* **2001**, 2460.
[27] W. Adam, P. L. Alsters, R. Neumann, C. R. Saha-Möller, D. Sloboda-Rozner, R. Zhang, *Synlett* **2002**, 2011.
[28] W. Adam, P. L. Alsters, R. Neumann, C. R. Saha-Möller, D. Sloboda-Rozner, R. Zhang, *J. Org. Chem.* **2003**, *68*, 1721.
[29] K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, *Science* **2003**, *300*, 964.
[30] K. Kamata, K. Yamaguchi, S. Hikichi, N. Mizuno, *Adv. Synth. Catal.* **2003**, *345*, 1193.
[31] See the Supporting Information (Table S1).
[32] H. Mimoun, I. S. De Roch, L. Sajus, *Tetrahedron* **1970**, *26*, 37.
[33] K. B. Sharpless, R. C. Michaelson, *J. Am. Chem. Soc.* **1973**, *95*, 6136.
[34] K. B. Sharpless, T. R. Verhoeven, *Aldrichimica Acta* **1979**, *12*, 63.
[35] T. Ito, K. Jitsukawa, K. Kaneda, S. Teranishi, *J. Am. Chem. Soc.* **1979**, *101*, 159.
[36] W. Adam, R. Kumar, T. I. Reddy, M. Renz, *Angew. Chem.* **1996**, *108*, 578; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 533.
[37] Water/acetonitrile (1:2 *v*/*v*) was also used for the epoxidation to solubilize both the catalyst **I** and allyl acetate. The reaction conditions were as follows: Substrate (5 mmol), **I** (20 μmol), 30% aq. H_2O_2 (5 mmol), water/acetonitrile (2+4 mL), 305 K, 24 h. The epoxidation of allyl acetate did not proceed at all, while that of **1a** proceeded to give a 26% yield of **1b** under the above conditions. Therefore, we conclude that the complete lack of epoxidation reactivity of allyl acetate is not caused by the low solubility into an aqueous phase.
[38] W. Adam, C. M. Mitchell, C. R. Saha-Möller, *J. Org. Chem.* **1999**, *64*, 3699.
[39] The effect of methanol on the epoxidation of **1a** was examined. As shown in Figure S7, the epoxidation was inhibited by the co-existence of methanol and was completely inhibited in the methanol solvent, suggesting that binding of an alcohol functional group to **I** is a key step in Scheme 1.
[40] The signals at δ 1.44 and 5.35 sharply increased followed by the increase in the signals at δ 2.21 and 9.79. The signal at δ 2.04 (s) appeared with an induction period and can be assigned to acetic acid. The ^1H and ^{13}C NMR spectra of the reaction solution of **I** (50 mM) with **1a** (870 mM) in D_2O in the range of 278–305 K showed only resonances of **1a** and **1b**, and no resonances due to tungsten-alcoholate species were observed.
[41] W. Clegg, R. J. Errington, P. Kraxner, C. Redshaw, *J. Chem. Soc. Dalton Trans.* **1992**, 1431.
[42] D. V. Baxter, M. H. Chisolm, S. Doherty, N. E. Gruhn, *Chem. Commun.* **1996**, 1129.
[43] G. G. Allan, A. N. Neogi, *J. Catal.* **1970**, *16*, 197.
[44] D. V. Deubel, *J. Phys. Chem. A* **2001**, *105*, 4765.
[45] N. J. Cambell, A. C. Dengel, C. J. Edwards, W. P. Griffith, *J. Chem. Soc. Dalton Trans.* **1989**, 1203.
[46] S. Krishnamurthy, H. C. Brown, *J. Org. Chem.* **1975**, *40*, 1864.
[47] S. Krishnamurthy, H. C. Brown, *J. Org. Chem.* **1977**, *42*, 1197.
[48] B. Morgan, A. C. Oehlschlager, T. M. Stokes, *J. Org. Chem.* **1992**, *57*, 3231.
[49] H. O. House, S. S. Ro, *J. Am. Chem. Soc.* **1958**, *80*, 2428.
[50] W. Adam, M. Braun, A. Griesbeck, V. Luccini, E. Staab, B. Will, *J. Am. Chem. Soc.* **1989**, *111*, 203.
[51] M. J. Kurth, M. A. Abreo, *Tetrahedron* **1990**, *46*, 5085.
[52] H. Pettersson, A. Gogoll, J.-E. Bäckvall, *J. Org. Chem.* **1992**, *57*, 6025.
[53] H. Fuji, K. Oshima, K. Utimoto, *Chem. Lett.* **1992**, 967.
[54] D. F. Taber, J. B. Houze, *J. Org. Chem.* **1994**, *59*, 4004.
[55] D. C. Dittmer, Y. Zhang, R. P. Discordia, *J. Org. Chem.* **1994**, *59*, 1004.
[56] Y. F. Zheng, D. S. Dodd, A. C. Oehlschlager, P. G. Hartman, *Tetrahedron* **1995**, *51*, 5255.
[57] W. Adam, A. Corma, T. I. Reddy, M. Renz, *J. Org. Chem.* **1997**, *62*, 3631.

Received: April 9, 2004
Published online: August 6, 2004

