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Aust. J. Chem. **2009**, *62*, 947

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Yong Ding, Baochun Ma, Dejie Tong, Hui Han, and Wei Zhao

(Vol. 62, no. 7, pp. 739–746)

The publisher wishes to apologize for the error that appeared in the spelling of the names of the authors for Volume 62, issue 7 for the above article.

The correct spelling should have read:

Yong Ding, Baochun Ma, Dejie Tong, Hui Hua, and Wei Zhao

10.1071/CH08547_CO 0004-9425/09/080947

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Synthesis of Epoxides Catalyzed by a Halide-Free Reaction-Controlled Phase-Transfer Catalytic System: $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]/H_2O_2$/Dioxan/Olefin

Yong Ding,[A,B] *Baochun Ma,*[A] *Dejie Tong,*[A] *Hui Han,*[A] *and Wei Zhao*[A]

[A]State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China.

[B]Corresponding author. Email: dingyong1@lzu.edu.cn

The epoxidation of alkenes was successfully catalyzed by a recyclable catalytic system: $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]/H_2O_2$/dioxan/olefin. This new catalytic system is not only capable of catalyzing homogeneous epoxidation of alkenes with a unique reaction-controlled phase-transfer character, but also avoids the use of chlorinated solvents. The reactions were conducted in a biphasic mixture of aqueous H_2O_2/dioxan, and many kinds of alkenes could be efficiently converted to the corresponding epoxides in high yields. Both new and used $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]$ catalyst was characterized by ^{31}P magic angle spin NMR, and IR.

Manuscript received: 15 December 2008.
Final version: 15 April 2009.

Introduction

Epoxides are highly useful intermediates for the manufacture of a range of important commercial products, and epoxidation of alkenes is among the most important reactions in organic synthesis. The oxidation of alkenes with aqueous hydrogen peroxide is very attractive from the viewpoint of industrial production and synthetic organic chemistry because aqueous hydrogen peroxide is cheap, environmentally clean, and easy to handle.[1–8] Soluble transition metal-based catalysts containing tungsten, manganese, molybdenum, and rhenium have been developed for oxidation with aqueous H_2O_2. Among them, tungsten-based catalysts including polyoxometalates show a high efficiency of H_2O_2 utilization and a high selectivity in forming the epoxides. Many groups[8–30] have been involved in this research topic in the world, and in particular, the groups of Venturello and Ishii have contributed significantly to the development of tungsten-based catalysts. In 1983, Venturello et al.[9,10] reported an efficient epoxidation of alkenes with a dilute H_2O_2 solution (15%) as oxidant using a complex consisting of tungstate and phosphate as catalyst. A combination of $H_3PW_{12}O_{40}$ and cetylpyridinium chloride was then developed in 1988 by Ishii et al.[11] for epoxidation of alkenes using a commercially available H_2O_2 solution (35%) as oxidant.

Subsequently, many improvements based on tungsten-based catalysts were developed,[12–20] such as Noyori's[12] halide-free method and the divacant lacunary silicotungstate epoxidation system of Mizuno.[13] Despite the high activity and excellent selectivity obtained in epoxidation of alkenes using improved catalysts, difficulty in recovery and reuse of those homogeneous metal species has restricted their wide application in industrial and laboratory synthesis. Xi[21–23] explored a reaction-controlled phase-transfer catalyst to resolve the problem of recovery of catalyst; however, Xi's catalytic system used toxic mixed solvents (trimethylbenzene and trioctylphosphate) and carcinogenic chlorocarbons (chloroform and 1,2-dichloroethane) as solvents.

Here, we report our preliminary results on research in which a new tungsten-based polyoxometalate, $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]$ **1** was synthesized and used as reaction-controlled phase-transfer catalyst for the epoxidation of alkenes with H_2O_2 as the oxidant and dioxan as the solvent. This system can be used for the homogeneous catalytic epoxidation of olefins using H_2O_2 as the oxidant, and exhibits high conversion and selectivity. After reaction, the catalyst can be precipitated from the solvents and reused just like a heterogeneous catalyst. Therefore, this catalytic system possesses the advantages of both homogeneous and heterogeneous catalysts.

Results and Discussion

Catalytic Reaction

Table 1 summarizes the catalytic epoxidation of 1-octene in dioxan with 30% H_2O_2 using different catalysts. It was found that the epoxidation does occur with all the catalysts, but the yield of 1,2-epoxyoctane depends on the different organic counter-cations of heteropolyoxotungstates and anions of the quaternary ammonium salts that were used to prepare the catalysts. Some catalysts containing a small quaternary ammonium cation, such as tetrabutyl ammonium, were insoluble in the reaction system during epoxidation, so the yield of epoxide was low (entries 3 and 4). The catalysts containing a bigger quaternary ammonium cation, such as dioctadecyldimethyl ammonium and dodecylpyridinium, were reaction-controlled phase-transfer catalysts with high activity and selectivity (entries 1 and 2). The activity of catalysts synthesized with quaternary ammonium bromide was inferior to that prepared with quaternary ammonium chloride (entries 5 and 6). Hence, the structure

10.1071/CH08547 0004-9425/09/070739

Table 1. Epoxidation of 1-octene with different catalysts

Reaction conditions: 1.5 mmol alkene; 0.75 mmol H_2O_2; 0.01 mmol catalyst; 3 mL dioxan; reaction temperature: 60°C, reaction time: 2 h. Selectivity [%] = epoxide [mol]/all products [mol]. Yield [%] = products [mol]/H_2O_2 used [mol] × 100. Conversions and selectivities were determined by gas chromatography using an internal standard technique and were based on H_2O_2. The products were identified by GC-MS

Entry	Catalyst	Selectivity [mol-%]	Yield [mol-%]
1[A]	$([CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]$	99	97
2[A]	$[\pi\text{-}C_5H_5N(CH_2)_{11}CH_3]_3[PW_4O_{32}]$	99	89
3[A]	$[(CH_3(CH_2)_3)_4N]_3[PW_4O_{32}]$	99	3
4[A]	$[C_6H_5CH_2N(CH_3)_3]_3[PW_{12}O_{40}]$	99	4
5[B]	$[\pi\text{-}C_5H_5N(CH_2)_{13}CH_3]_3[PW_4O_{28}]$	99	49
6[B]	$[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{28}]$	74	26
7	$[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_{12}O_{40}]$	99	8
8	$[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_{12}O_{40}]$	99	6
9	$[\pi\text{-}C_5H_5N(CH_2)_{11}CH_3]_3[PW_{12}O_{40}]$	99	1
10	None	0	0
11[C]	$[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]$	99	2

[A] Quaternary ammonium chloride salts are quaternary ammonium chloride salts.

[B] Quaternary ammonium chloride salts are quaternary ammonium bromide salts.

[C] No H_2O_2 was added in the reaction.

and anion of the quaternary ammonium salts play an important role on forming an efficient reaction-controlled phase-transfer catalyst. All the catalysts $[\pi\text{-}C_5H_5N(CH_2)_{11}CH_3]_3[PW_{12}O_{40}]$, $[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_{12}O_{40}]$, and $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_{12}O_{40}]$ showed poor activity for the epoxidation of 1-octene in dioxan (entries 7, 8, and 9), indicating the catalyst $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]$ is different from $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_{12}O_{40}]$ in essence.

The results of the epoxidation of 1-octene catalyzed by heteropolyoxotungstate $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]$ (**1**) with different solvents is summarized in Table 2. It was shown that the yields of epoxidation are highest in the solvents *tert*-butanol, 1,2-dichloroethane and dioxan. The epoxidation yield was poor when using other solvents such as heptane, ethanol, and acetonitrile. Although the solvent *tert*-butanol was good for the epoxidation of 1-octene, the recovery of catalyst **1** was poor and the yield of epoxide was only 48% for the second cycle. The solvent 1,2-dichloroethane is toxic and carcinogenic. Therefore, we selected dioxan as the best solvent to carry out other experiments.

The epoxidation of various alkenes catalyzed by **1** is shown in Table 3. For example, when catalytic epoxidations of olefins were performed at 60°C with H_2O_2 in a dioxan solvent/aqueous biphasic system, the conversions were 98 and 99% based on H_2O_2 and the selectivities were 99 and 99% for 1-octene and cyclooctene, respectively.

When using 30% H_2O_2 to carry out the epoxidation of olefins, catalyst **1** precipitates from the reaction medium after epoxidation and can be recovered and reused. In an aqueous dioxan biphasic system, catalyst **1** itself is not soluble in the organic solvent phase, but it dissolves slowly under the action of H_2O_2 and the increase in reaction temperature, which subsequently leads to homogeneous catalytic epoxidation of olefins. During the reaction, the system gradually changes from turbid to clear. When the reaction stops and the temperature drops, catalyst **1** precipitates gradually. As a result, the system becomes turbid again, indicating completion of the epoxidation.

Table 2. Epoxidation of 1-octene with catalyst 1 under different solvent conditions

Reaction conditions: 1.5 mmol alkene; 0.75 mmol H_2O_2; 0.01 mmol catalyst **1**; 3 mL solvent; reaction temperature: 60°C, reaction time: 2 h. Yield [%] = products [mol]/H_2O_2 used [mol] × 100. Conversions and selectivities were determined by gas chromatography using an internal standard technique and were based on H_2O_2

Entry	Solvent	Conversion [mol-%]	Yield [mol-%]
1	Cyclohexane	78	77
2	Heptane	46	45
3	Ethanol	46	45
4	*tert*-Butanol	99	98
5	*iso*-Butyl alcohol	48	47
6	Toluene	44	43
7	Acetonitrile	38	37
8	THF	57	56
9	1,2-Dichloroethane	99	98
10	Dioxan	98	97

This phenomenon displays a solid–liquid–solid phase transfer of catalyst **1** that is controlled by the reaction conditions, and so these catalysts are called reaction-controlled phase-transfer catalysts.

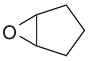
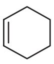
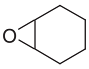
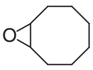
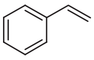
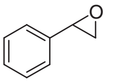
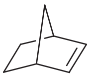
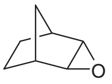
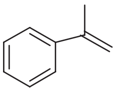
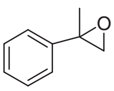
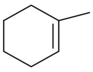
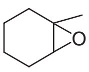
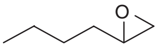
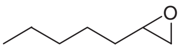
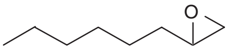
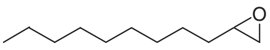
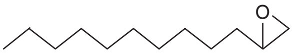
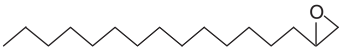
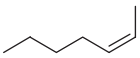
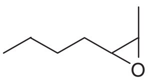
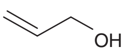
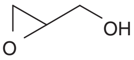
The heteropolyoxotungstate catalyst **1** could be applied to the epoxidation of various olefins (such as linear terminal olefins, internal olefins, cyclic olefins, styrene, and unactivated alkenes) with 30% H_2O_2 (Table 3). Excellent catalytic activity and selectivity, as well as the same property of reaction-controlled phase-transfer catalysis, were also observed in the epoxidation of such olefins. Bulky cyclic olefins, such as cyclohexene, styrene, cyclooctene, and norbornene, were epoxidized with ~95% yield of epoxides. Non-activated terminal C_7–C_{16} alkenes such as 1-heptene, 1-octene, 1-undecene, 1-dodecene, and 1-hexadecylene could be transformed to the corresponding epoxide specifically in ~85% yield after 2 h reaction. For the epoxidation of *cis*-2-heptene, the configuration around the C=C bond was retained in the corresponding epoxide (*cis*-2,3-epoxyheptane was obtained in 95% yield). In general, the epoxidation of allylic alcohols is more difficult compared with the epoxidation of cyclic olefins, because the C=C double bond in allyl alcohols is rendered relatively electron-deficient by the electron-withdrawing hydroxyl group (–OH). A 74% yield of 2,3-epoxy-1-propanol was obtained with catalyst **1** in dioxan, indicating this epoxidation system is fairly universal to all kinds of alkenes.

The $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]/H_2O_2$/dioxan catalytic system was also effective for epoxidation of dienes (Table 4). After a 2-h reaction, conversion of 99% for all substrates was obtained, but the selectivity for monoepoxides was not high enough. Only 4-vinyl-1-cyclohexene and limonene, a C=C moiety with higher electron density, were epoxidized regioselectively to give the corresponding monoepoxide without the successive epoxidation of the other C=C fragment (entries 1 and 5).

To evaluate the stability and reuse of the solid $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]$ catalyst, we investigated the epoxidation of cyclohexene with the **1**/H_2O_2/dioxan system (Table 5). The solid catalyst can be easily recovered by filtration and dried in air. After the catalytic epoxidation of cyclohexene in the **1**/H_2O_2/dioxan system, catalyst **1** is self-precipitated with a 90% recovery yield (by weight). From Table 5, after four consecutive cycles of the reaction, an 80% yield of the epoxide with

Table 3. Epoxidation of various olefins catalyzed by 1 in dioxan with 30% H_2O_2

Reaction conditions: 1.5 mmol alkene; 0.75 mmol H_2O_2; 0.01 mmol catalyst **1**; 3 mL dioxan; reaction temperature: 60°C, reaction time: 2 h. Selectivity [%] = epoxide [mol]/all products [mol]. Yield [%] = products [mol]/H_2O_2 used [mol] × 100. Conversions and selectivities were determined by gas chromatography using an internal standard technique and were based on H_2O_2

Substrate	Product	Selectivity [mol-%]	Yield [mol-%]
		95	88
		98	97
		99	98
		97	96
		96	95
		98	97
		99	98
 A		98	70
 B		97	83
		99	97
		98	80
		97	87
		98	84
		96	95
		99	74

[A]Reaction time 5 h. [B]Reaction time 3 h.

99% selectivity was still obtained for the epoxidation of cyclohexene in this catalytic system, but the epoxide yield decreased gradually from cycle to cycle. The decrease of the catalyst activity can be attributed to the leaching of W after each catalytic run. The reason for the catalyst could be recovered after the reaction can be attributed to the use of the solvent dioxan and the reaction temperature.

^{31}P MAS NMR Analysis

The ^{31}P magic angle spin (MAS) NMR spectrum of our fresh catalyst **1** (Fig. 1a) gives several broad peaks and suggests that the catalyst is a mixture that contains several different phosphorus-containing species. The lines at 3.9 and 1.1 ppm perhaps can be attributed to $[(PO_4)(WO(O_2)_2)_4]^{3-}$ and $[(PO_4)(WO(O_2)_2)_2(WO(O_2)_2(H_2O))]^{3-}$, respectively.[15,22,23] We cannot determine what these species are only according to the ^{31}P MAS NMR spectra, because this catalyst is a mixture and is complex. The clear assignment of different phosphorus-containing species needs a combination of several characterization techniques. The ^{31}P MAS NMR spectrum of the catalyst of cycle 1 (Fig. 1b) exhibits four peaks at 0.3, −12.6, −14.3, and −15.3 ppm. The line at 0.3 ppm can be attributed to

Table 4. Epoxidation of dienes catalyzed by 1

Reaction conditions: 1.5 mmol alkene; 0.75 mmol H_2O_2; 0.01 mmol catalyst **1**; 3 mL dioxan; reaction temperature: 60°C, reaction time: 2 h. Yield [%] = products [mol]/H_2O_2 used [mol] × 100. Conversions and selectivities were determined by gas chromatography using an internal standard technique and were based on H_2O_2

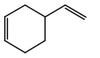
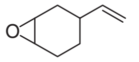
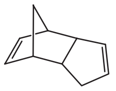
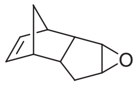
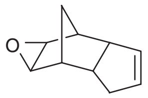
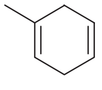
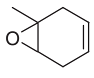
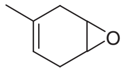
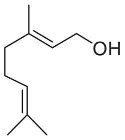
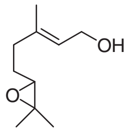
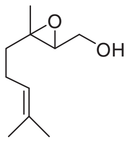
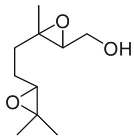
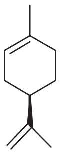
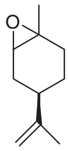
Entry	Dienes	Product	Selectivity [mol-%]	Yield [mol-%]
1			99	95
2			63	55
			36	32
3			55	54
			45	44
4			29	24
			55	46
			15	13
5			99	98

Table 5. Epoxidation of cyclohexene with catalyst 1 for different reuse cycles

Reaction conditions: 1.5 mmol cyclohexene; 0.75 mmol H_2O_2; 0.01 mmol catalyst **1**; 3 mL dioxan; reaction temperature: 60°C, reaction time: 2 h. Selectivity [%] = epoxide [mol]/all products [mol]. Yield [%] = products [mol]/H_2O_2 used [mol] × 100

No. of cycle times	Conversion [mol-%]	Selectivity [mol-%]	Yield [mol-%]
1	99	99	98
2	90	99	89
3	84	99	83
4	81	99	80

species with a low W/P ratio, and the lines at −12.6, −14.3, and −15.3 ppm can be attributed to the lacunar Keggin-type structure of the $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_7[PW_{11}O_{39}]$ and complete Keggin-type structure $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_{12}O_{40}]$, respectively. The formation of some Keggin-type species after epoxidation may explain the precipitation of catalyst from the reaction solvent. As can be seen from Fig. 1, the ^{31}P MAS NMR spectrum of Xi's catalyst synthesized in the present laboratory (Fig. 1d) is different from that of catalyst **1** (Fig. 1a). The fresh Xi's catalyst shows several broad peaks, suggesting that the catalyst is a mixture of several different polytungstophosphate species. It is difficult to assign these phosphorus-containing

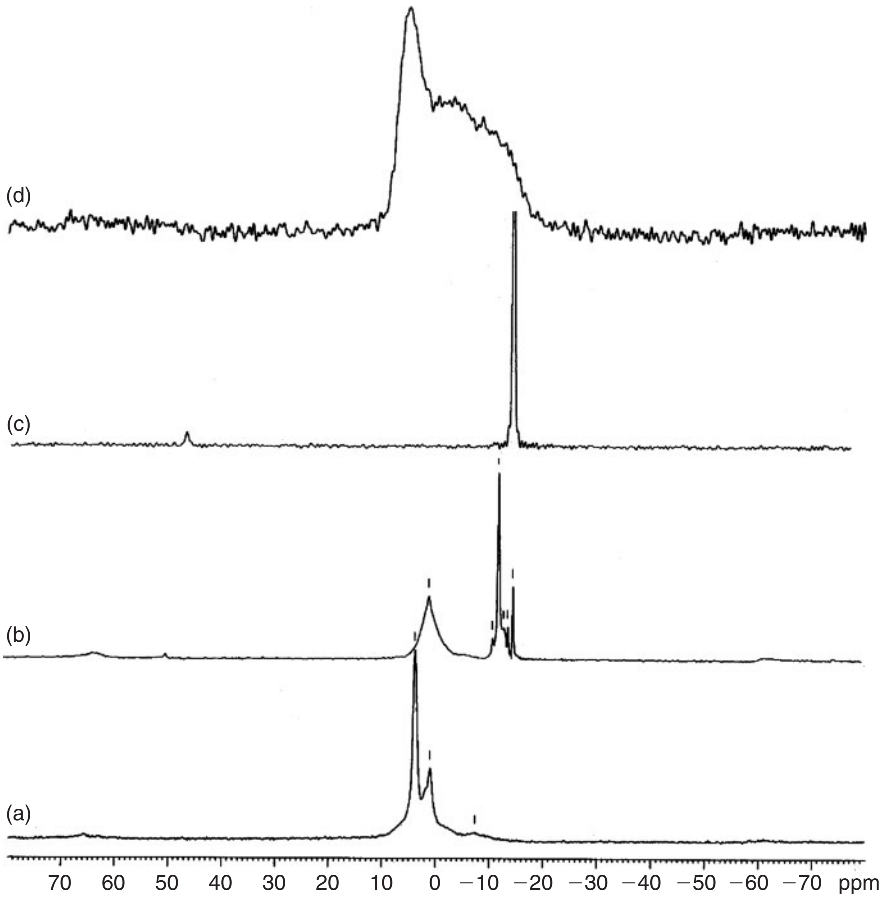


Fig. 1. ^{31}P MAS NMR spectra of: (a) the fresh catalyst $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]$; (b) the catalyst of cycle 1; (c) the catalyst $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_{12}O_{40}]$; (d) Xi's fresh catalyst $[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{16}]$.

species to those of clearly identified phosphatooxotungstate species.

IR Analysis

It can be seen that there are distinguishing differences in the IR spectra between the fresh catalyst $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]$ and the used one. The Fourier-transform (FT)-IR spectrum of the fresh catalyst (see Fig. 2a) gives bands at 1092, 1057, 983, 900, 847, 787, 722, 683, 651, 574, 548, 524, and 442 cm^{-1} in the fingerprint region. Infrared spectra show that the fresh catalyst **1** does have a strong peroxo-bond absorption peak ν(O–O) at 847 cm^{-1}, but the peroxo-bond disappears in the recovered catalyst (see Fig. 2b). Compared with the IR spectrum of fresh catalyst, the bands of used catalyst indicate a change into another species and are fairly similar to those of $[PW_{11}O_{39}]^{7-}$ and $[PW_{12}O_{40}]^{3-}$ with a Keggin structure.[22,23] The vibrational regions of ν(W=O), ν(W–O$_b$–W), and ν(W–O$_c$–W) appear at 950, 890, and 822 cm^{-1}, respectively, for the recycled catalyst.

When the catalyst contacts hydrogen peroxide during the epoxidation process, the catalyst becomes soluble with the help of the counter-cation dioctadecyldimethyl ammonium as a phase-transfer agent in organic solvent. The active species reacts with the substrate and transfers active oxygen to the double bond of the alkenes. With the continuous consumption of hydrogen peroxide, those smaller anions polymerize into larger anions, forming the W–O$_b$–W and W–O$_c$–W bonds, such as in $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_7[PW_{12}O_{40}]$ and polytungstophosphate species with a low W/P ratio (see Fig. 1b). Furthermore, the reaction temperature greatly influences the solubility of the catalyst. With the increase of reaction temperature, the catalyst gradually dissolves and catalyzes the epoxidation in a homogeneous mode, then precipitates from the reaction medium as the reaction temperature drops after the reaction. Consequently, the catalyst becomes an insoluble solid and precipitates from the reaction medium.

Comparison with Other Epoxidation Catalysts

Table 6 lists the epoxidation of 1-octene with some different catalytic tungsten-based polyoxometalatecatalysts systems. The procedure for 1-octene epoxidation in Venturello[9] used a system of a Na_2WO_4–H_3PO_4–quaternary ammonium chloride combined catalyst and 1,2-dichloroethane as solvent, giving the 1,2-epoxyoctane product in 81% yield after 1-h reaction. Ishii[11] made progress by using $H_3PW_{12}O_{40}$ and *N*-cetylpyridinium chloride in a chloroform/water mixture, resulting in a yield of 80%. However, both of these require toxic and carcinogenic chlorinated hydrocarbon solvents to obtain a high yield and high selectivity (yield was only 33% in refluxing benzene[11]), defeating the environmental and economic advantages of H_2O_2 as the oxidant. The epoxidation systems of Venturello–Ishii has two drawbacks: (a) the use of toxic and carcinogenic chlorocarbons (chloroform and 1,2-dichloroethane) as the solvents; (b) the difficulties of separating and reusing the catalysts.

A high yield (94% for 1,2-epoxyoctane) for the epoxidation of 1-octene was reported in Noyori's epoxidation system,[12] but the procedure was performed at ~90°C. The activity is

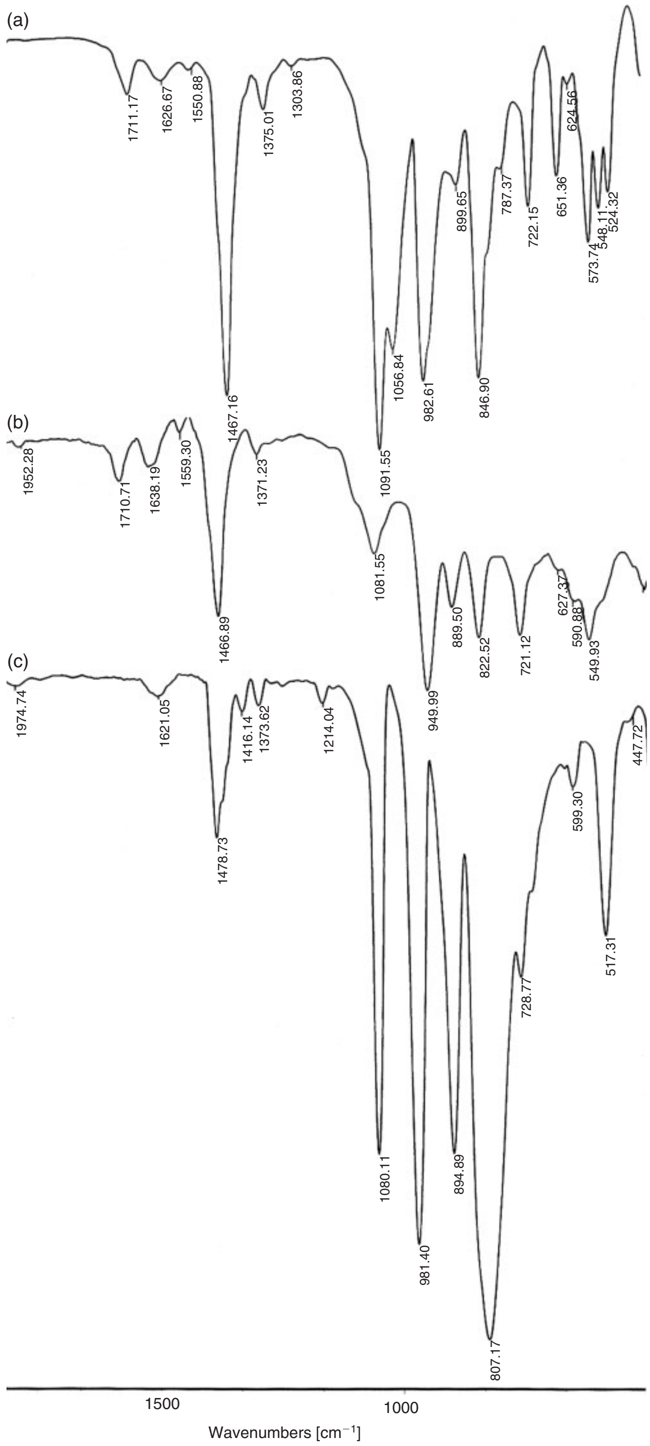


Fig. 2. Infrared spectra of: (a) fresh catalyst $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]$; (b) the catalyst of cycle 1; (c) the catalyst $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_{12}O_{40}]$.

raised by increasing the temperature (90°C); this is not a good option for epoxidation owing to the hydrolytic ring-opening of epoxides. Note that the reagent of (aminomethyl)phosphonic acid ($NH_2CH_2PO_3H_2$) and phase transfer reagent of methyltri-*n*-octylammonium hydrogensulfate ($[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$) are very expensive.

Although the reaction temperature was low (32°C) and the yield of epoxide was high (90%) in the divacant lacunary silicotungstate ($[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}](Bu_4N)_4$) epoxidation system reported by Mizuno,[13] difficulty of recovery and reuse of the homogeneous metal species has restricted their wide application in industrial and laboratory syntheses.

The yield of 1,2-epoxyoctane was relatively low (79%) in Xi's catalytic system.[24] In addition, Xi did not report the recycling result of the epoxidation of 1-octene although he reported his system can resolve the problem of the recovery of the catalyst.

Our $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]$ catalyst showed the best activity in the epoxidation of 1-octene among the catalysts in Table 6; a 97% yield of 1,2-epoxyoctane was obtained after 2 h at 60°C. Furthermore, catalyst **1** could be recycled many times and the epoxidation was carried out in halide-free conditions (dioxan as solvent).

Conclusions

In conclusion, we have developed a halide-free reaction-controlled phase-transfer catalytic system consisting of $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]/H_2O_2$/dioxan, and can efficiently catalyze many kinds of alkene epoxidation in high yield with an environmentally benign character. The catalyst could be recovered and reused after reaction. This halide-free catalytic system overcomes the drawbacks of previously reported tungsten-based catalysts, which were difficulty to recover, and the use of toxic and carcinogenic chlorocarbons as solvents.

Experimental

Catalyst Preparation

$[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]$ **1**

$H_3PW_{12}O_{40}$ (3.0 g, ∼1.0 mmol) in 30% H_2O_2 (10 mL) was added dropwise to a solution of dioctadecyldimethyl ammonium chloride (1.78 g, 3.1 mmol) in 30% H_2O_2 (40 mL) with intense stirring over 30 min. A white precipitate was produced by the reaction of the three reactants above, and the mixture was stirred at 40°C for 6 h. The suspended mixture was cooled to room temperature. After filtration, the precipitate was washed repeatedly with water and dried under air. Catalyst **1** was obtained as a white powder. Yield: 2.1 g (90%). (Anal. calc. for $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]$: C 46.72, H 8.20, N 1.43, P 1.06, W 25.11. Found: C 46.16, H 8.39, N 1.54, P 1.02, W 25.35%.) ν_{max}(KBr)/cm^{-1} 1092, 1057, 983, 900, 847, 787, 722, 683, 651, 574, 548, 524, and 442. δ_P (MAS) 3.9, 1.1, −7.3.

Catalysts $[\pi\text{-}C_5H_5N(CH_2)_{11}CH_3]_3[PW_4O_{32}]$, $([CH_3(CH_2)_3]_4N)_3[PW_4O_{32}]$ and $[C_6H_5CH_2N(CH_3)_3]_3[PW_{12}O_{40}]$ were synthesized with quaternary ammonium chloride as counter-cation. Catalysts $[\pi\text{-}C_5H_5N(CH_2)_{13}CH_3]_3[PW_4O_{28}]$ and $[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{28}]$ were synthesized using quaternary ammonium bromide as counter-cation. Other synthetic steps were similar to the above method for catalyst $[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]$.

$[\pi\text{-}C_5H_5N(CH_2)_{11}CH_3]_3[PW_4O_{32}]$: (Calc. for $C_{51}H_{90}N_3PW_4O_{32}$: C 30.24, H 4.45, N 2.08, P 1.53, W 36.34. Found: C 31.28, H 4.26, N 1.87, P 1.24, W 35.70%.) ν_{max}(KBr)/cm^{-1} 1214, 1175, 1079, 1029, 951, 895, 843, 823, 775, 720, 686, 646, 630, 571, 549, 524, 448. δ_P (MAS) 4.8, 1.8, −7.6, −15.9.

$([CH_3(CH_2)_3]_4N)_3[PW_4O_{32}]$: (Anal. calc. (%) for $C_{16}H_{36}N_3PW_4O_{32}$: C 12.40, H 2.32, N 2.71, P 2.00. Found: C 11.88, H 2.26, N 2.87, P 1.93%.) ν_{max}(KBr)/cm^{-1} 1152, 1085, 1054, 975, 896, 844, 818, 741, 651, 621, 596, 576, 549, 522, 457. δ_P (MAS) 3.4, 2.5, −15.5.

$[C_6H_5CH_2N(CH_3)_3]_3[PW_{12}O_{40}]$: (Anal. calc. for $C_{30}H_{48}N_3PW_{12}O_{40}$: C 10.82, H 1.44, N 1.26. Found: C 10.13, H 1.57,

Table 6. Comparison of the epoxidation of 1-octene with different catalytic systems

Catalyst system	Catalyst composition	Reaction time [h]	Reaction temperature [°C]	Solvent	Yield [mol-%]
Present system[A]	$[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_4O_{32}]$ (**1**)	2	60	Dioxan	97
Venturello[B]	$Na_2WO_4 + H_3PO_4$ + quaternary ammonium chloride	1	70	1,2-Dichloroethane	81
Ishii[C]	$H_3PW_{12}O_{40}$ + cetylpyridinium chloride	5	60	Chloroform	80
Noyori[D]	$Na_2WO_4{\cdot}2H_2O + NH_2CH_2PO_3H_2 + [CH_3(n\text{-}C_8H_{17})_3N]HSO_4$	4	90	Toluene	94
Mizuno[E]	$[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}](Bu_4N)_4$	10	32	MeCN	90
Xi[F]	$[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{16}]$	7	45	Mixed solvent[G]	79

[A] Present paper; [B] ref. [10]; [C] ref. [11]; [D] ref. [12]; [E] ref. [13]; [F] ref. [24]. [G] Trimethylbenzene and trioctylphosphate.

N 1.17%.) ν_{max}(KBr)/cm^{-1} 1479, 1080, 981, 895, 807, 729, 599, 517. δ_P (MAS) 2.1, −15.0.

$[\pi\text{-}C_5H_5N(CH_2)_{13}CH_3]_3[PW_4O_{28}]$: (Anal. calc. for $C_{57}H_{102}N_3PW_4O_{28}$: C 33.49, H 4.99, N 2.06, P 1.52. Found: C 33.87, H 4.77, N 1.97, P 1.46%.) ν_{max}(KBr)/cm^{-1} 1174, 1080, 953, 890, 821, 774, 722, 685, 645, 594. δ_P (MAS) 6.1, −1.3, −7.7, −13.2, −15.8, −23.4.

$[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{28}]$: (Anal. calc. for $C_{63}H_{114}N_3PW_4O_{28}$: C 35.55, H 5.36, N 1.98, P 1.46. Found: C 35.77, H 5.17, N 1.77, P 1.42%.) ν_{max}(KBr)/cm^{-1} 1486, 1173, 1078, 978, 896, 809, 679, 596, 521. δ_P (MAS) 6.3, −1.6, −5.7, −13.0, −15.2, −16.1.

$[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_{12}O_{40}]$: To a solution of cetylpyridinium bromide (5.2 mmol) in distilled water (70 mL) was added dropwise $H_3PW_{12}O_{40}$ (1.7 mmol) in distilled water (10 mL) with stirring at ambient temperature and a white precipitate formed immediately. After being stirred continuously for 3.5 h, the resulting mixture was filtered, washed several times with distilled water, and then dried at room temperature. ν_{max}(KBr)/cm^{-1} 1464, 1173, 1080, 978, 896, 830–740, 678, 522. δ_P (MAS) −15.4.

$[\pi\text{-}C_5H_5N(CH_2)_{11}CH_3]_3[PW_{12}O_{40}]$: To a solution of 1-dodecylpyridinium chloride (0.51 mmol) in distilled water (7 mL) was added dropwise $H_3PW_{12}O_{40}$ (0.17 mmol) in distilled water (1 mL) with stirring at ambient temperature to form a white precipitate immediately. After being stirred continuously for 3.5 h, the resulting mixture was filtered, washed several times with distilled water, and then dried at room temperature. ν_{max}(KBr)/cm^{-1} 1463, 1171, 1082, 979, 898, 832–741, 677, 520. δ_P (MAS) −15.3.

$[(CH_3(CH_2)_{17})_2N(CH_3)_2]_3[PW_{12}O_{40}]$: To a solution of dioctadecyldimethyl ammonium chloride (0.51 mmol) in distilled water (7 mL) was added dropwise $H_3PW_{12}O_{40}$ (0.17 mmol) in distilled water (1 mL) with stirring at ambient temperature and a white precipitate formed immediately. After being stirred continuously for 3.5 h, the resulting mixture was filtered, washed several times with distilled water, and then dried at room temperature. ν_{max}(KBr)/cm^{-1} 1467, 1171, 1081, 980, 896, 831–740, 678, 521. δ_P (MAS) −15.5.

$[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{16}]$ (Xi's catalyst) was synthesized by the method reported in ref. [22]. (Anal. calc. for C 39.08, H 5.95, N 2.17, P 1.60. Found: C 38.34, H 6.17, N 2.31, P 1.52%.) ν_{max}(KBr)/cm^{-1} 1087, 1032, 942, 884, 776, 719, 686, 625, 582, 543. δ_P (MAS) 4.9, −2.8, −10.1.

Characterization Techniques

Infrared spectra were recorded on a Nocolet FTIR-360 spectrometer. The catalysts were measured using 2–4% (w/w) KBr pellets prepared by manual grinding. ^{31}P MAS NMR spectra were recorded at 9.4 T on a Bruker Avance-400 wide-bore spectrometer. The ^{31}P MAS NMR spectra of solid catalyst with high-power proton decoupling were obtained at 161.9 MHz with a broad band MAS probe head using 4-mm ZrO_2 rotors, a 3.8-μs pulse, 30-s repetition time, and 128 scans, with samples spun at 10 kHz and referenced to 85% H_3PO_4. GC analyses were performed on a Shimadzu GC-9AM with a flame ionization detector equipped with an SE-54 capillary column (internal diameter 0.25 mm, length 30 m). GC-MS were recorded on a Finnigan Trace DSQ (Thermo Electron Corporation) at an ionization voltage of 70 eV equipped with a DB-5 capillary column (internal diameter 0.25 mm, film thickness 0.25 μm, length 30 m). Chemical elemental analysis of the catalysts was done on an inductively coupled plasma-atomic emission spectrometer (IRIS ER/S), and C, H, and N contents were measured on a Elementar Vario EL spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 and Varian Mercury 300 MHz spectrometer with TMS as an internal standard and $CDCl_3$ as solvent unless otherwise noted.

Catalytic Reaction

The catalytic reactions were performed in a 25-mL two-necked round-bottomed flask equipped with a septum, a magnetic stirring bar, and a reflux condenser. The epoxidation was carried out as follows: catalyst, solvent, substrate, and H_2O_2 (30% aq.) were placed in the reaction flask. The reaction was carried out at 333 K and detected by TLC accompanied with GC. After the reaction was over, the organic layer was analyzed by GC. The yield of products was calculated from the peak areas using an internal standard method. The epoxide products were identified by GC-MS (Finnigan Trace DSQ). At the same time, assignments of products were made by comparison with retention times of authentic samples. The carbon balance in each experiment was in the range of 95–100%. After reaction, the catalyst was precipitated from the solvent and was separated by centrifugation. For the blank reaction, no catalyst was added to the flask and other conditions were the same as above. For reactions in the absence of molecular oxygen, the reaction vessel was purged with argon and then capped with a rubber septum stopper. For reactions in the presence of molecular oxygen, the reaction vessel was not purged with argon or capped with a rubber septum.

For the characterization of diene products, the procedure was as follows:

The precipitate was removed by centrifugation and filtration, and the filtrate extracted with EtOAc (30 mL × 3); the organic layer was collected and washed with water and brine, then dried with anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (light petroleum/ethyl acetate, 10:1) to give epoxides as a colourless liquid. The structures of the epoxides were determined by EI MS, ^{1}H NMR, and ^{13}C NMR.

Acknowledgements

The present work was supported by the National Natural Science Foundation of China (grants no. 20702021 and 20803032). We gratefully thank Professor W. Wang for the measurement of solid-state NMR.

References

[1] X. M. Zhang, Z. R. Zhang, J. S. Suo, S. B. Li, *Catal. Lett.* **2000**, *66*, 175. doi:10.1023/A:1019007908847

[2] M. Klawonn, M. K. Tse, S. Bhor, C. Döbler, M. Beller, *J. Mol. Catal. A. Chem.* **2004**, *218*, 13. doi:10.1016/J.MOLCATA.2004.03.023

[3] B. Notari, *Adv. Catal.* **1996**, *41*, 253. doi:10.1016/S0360-0564(08)60042-5

[4] T. Sakamoto, C. Pac, *Tetrahedron Lett.* **2000**, *41*, 10009. doi:10.1016/S0040-4039(00)01787-1

[5] G. Grigoropoulou, J. H. Clark, J. A. Elings, *Green Chem.* **2003**, *5*, 1. doi:10.1039/B208925B

[6] D. Bogdal, M. Lukasiewicz, J. Pielichowski, S. Bednarz, *Synth. Commun.* **2005**, *35*, 2973. doi:10.1080/00397910500278479

[7] Y. Ding, Q. Gao, B. Wang, G. X. Li, L. Yan, J. S. Suo, *J. Porous Mater.* **2005**, *12*, 131. doi:10.1007/S10934-005-6770-2

[8] Y. Ding, W. Zhao, H. Hua, B. C. Ma, *Green Chem.* **2008**, *10*, 910. doi:10.1039/B808404A

[9] C. Venturello, E. Alneri, M. Ricci, *J. Org. Chem.* **1983**, *48*, 3831. doi:10.1021/JO00169A052

[10] C. Venturello, R. D'Aloisio, *J. Org. Chem.* **1988**, *53*, 1553. doi:10.1021/JO00242A041

[11] Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida, M. Ogawa, *J. Org. Chem.* **1988**, *53*, 3587. doi:10.1021/JO00250A032

[12] K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, R. Noyori, *J. Org. Chem.* **1996**, *61*, 8310. doi:10.1021/JO961287E

[13] K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, *Science* **2003**, *300*, 964. doi:10.1126/SCIENCE.1083176

[14] R. Neumann, M. Gara, *J. Am. Chem. Soc.* **1995**, *117*, 5066. doi:10.1021/JA00123A008

[15] C. Aubry, G. Chottard, N. Platzer, J. M. Bregeault, R. Thouvenot, F. Chauveau, H. Ledon, *Inorg. Chem.* **1991**, *30*, 4409. doi:10.1021/IC00023A024

[16] L. Salles, C. Aubry, R. Thouvenot, F. Robert, C. Doremieux-Morin, G. Chottard, H. Ledon, Y. Jeanin, J. M. Bregeault, *Inorg. Chem.* **1994**, *33*, 871. doi:10.1021/IC00083A008

[17] N. J. Campbell, A. C. Dengel, C. J. Edwards, W. P. Griffith, *J. Chem. Soc., Dalton Trans.* **1989**, 1203. doi:10.1039/DT9890001203

[18] D. C. Duncan, R. C. Chambers, E. Hecht, C. L. Hill, *J. Am. Chem. Soc.* **1995**, *117*, 681. doi:10.1021/JA00107A012

[19] Y. Ding, Q. Gao, G. X. Li, H. P. Zhang, J. M. Wang, L. Yan, J. S. Suo, *J. Mol. Catal. A. Chem.* **2004**, *218*, 161. doi:10.1016/J.MOLCATA.2004.04.019

[20] Y. Ding, B. C. Ma, Q. Gao, G. X. Li, L. Yan, J. S. Suo, *J. Mol. Catal. A. Chem.* **2005**, *230*, 121. doi:10.1016/J.MOLCATA.2004.12.017

[21] X. Zuwei, Z. Ning, S. Yu, L. Kunlan, *Science* **2001**, *292*, 1139. doi:10.1126/SCIENCE.292.5519.1139

[22] J. B. Gao, Y. Y. Chen, B. Han, Z. C. Feng, C. Li, N. Zhou, S. Gao, Z. W. Xi, *J. Mol. Catal. A. Chem.* **2004**, *210*, 197. doi:10.1016/J.MOLCATA.2003.09.018

[23] Y. Chen, J. Zhuang, X. Liu, J. Gao, X. Han, X. Bao, N. Zhou, S. Gao, Z. Xi, *Catal. Lett.* **2004**, *93*, 41. doi:10.1023/B:CATL.0000016947.14759.E9

[24] Z. W. Xi, H. P. Wang, Y. Sun, N. Zhou, G. Y. Cao, M. Li, *J. Mol. Catal. A* **2001**, *168*, 299. doi:10.1016/S1381-1169(00)00189-8

[25] Y. Ding, B. C. Ma, Q. Gao, J. S. Suo, *J. Chem. Res.* **2006**, 499.

[26] M. Hashimoto, K. Itoh, K. Y. Lee, M. Misono, *Top. Catal.* **2001**, *15*, 265. doi:10.1023/A:1016600601054

[27] W. Zhao, B. C. Ma, H. Hua, Y. Zhang, Y. Ding, *Catal. Commun.* **2008**, *9*, 2455. doi:10.1016/J.CATCOM.2008.06.013

[28] Y. Mahha, L. Salles, J. Y. Piquemal, E. Briot, A. Atlamsani, J. M. Brégeault, *J. Catal.* **2007**, *249*, 338. doi:10.1016/J.JCAT.2007.05.001

[29] D. Hoegaerts, B. F. Sels, D. E. de Vos, F. Verpoort, P. A. Jacobs, *Catal. Today* **2000**, *60*, 209. doi:10.1016/S0920-5861(00)00337-0

[30] T. Rüther, W. R. Jackson, A. M. Bond, *Aust. J. Chem.* **2002**, *55*, 691. doi:10.1071/CH02141