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ORIGINAL PAPER

# Novel Two-Phase Catalysis with Organometallic Compounds for Epoxidation of Vegetable Oils by Hydrogen Peroxide

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**Abstract** A series of new organometallic catalysts for epoxidized vegetable oils using $H_2O_2$ in a biphasic system were investigated. The effect of reaction parameters such as the amount of hydrogen peroxide, reaction time and temperature in the epoxidation of soybean oil are discussed in detail. A selectivity of 83.8% was obtained in 4 h at 60 °C, when $[(C_{18}H_{37})_2N(CH_3)_2]_3\{PO_4[WO(O_2)_2]_4\}$ was used as the catalyst. When methyltrioxorhenium (MTO), imidazole and $CH_3CN$ were used as the catalyst, adduct, and solvent respectively, a selectivity of 99.90% was achieved in 4 h at 20 °C. The catalytic system was used for the epoxidation of other oils, whose results showed it was active in the epoxidation of long-chain unsaturated compounds. Furthermore, the reaction of $H_2O_2$ with methyltrioxorhenium was studied by UV–Vis spectroscopy, which revealed the active peroxorhenium complexes formed during the reaction. Epoxidation of these oils with organometallic compounds occurred through the interactions between the oils unsaturated sites HOMO $\pi$(C–C) and the unoccupied peroxo $\sigma^*$(O–O) orbital.

**Keywords** Fats and oils · Liquid phase epoxidation · Peroxo-organometallic compounds · Peroxorhenium complexes · Peroxophosphatotungstate

## Introduction

Petroleum products are used widely throughout the world, and new research results addressing the global problems involved appear daily [1–4]. Recently, reviews [4–6] have summarized the state of the art in biological product (such as oils and fats) research. Vegetable oils are the important renewable raw materials in the chemical industry. And many chemical and biochemical reactions have been used for their conversion into value-added products to enhance oil's reactivity.

Among those reactions, epoxidation plays a significant role, since epoxidized vegetable oils and fatty acid derivatives are widely utilized in the plastics industry [7]. For example, they are starting materials for the production of epoxy resins as well as plasticizers and stabilizers for PVC resins to improve flexibility, elasticity, and toughness and also to impart heat and light stability to the polymer [8].

Traditionally, epoxidation of vegetable oils is conducted with carboxylic acid (such as formic acid, acetic acid and so on). However, this procedure causes several concerns about safety and engenders corrosion problems that are interrelated to the percarboxylic acids used. Additionally, the carboxylic acid processes have low selectivity and hazards associated with handling the peracids and serious pollution on an industrial scale [9].

Two-phase catalysis is becoming an area of environmentally friendly chemistry: the amount of catalytic species in the product phase must be negligible to allow its easy separation. Organometallic compounds can meet this requirement.

Nowadays, organometallic compounds [10] which are developed to epoxidize olefins mainly contain two kinds of compounds, namely, peroxophosphatotungstate and methyltrioxorhenium (MTO). Besides, their use as catalyst in the

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liquid phase epoxidation has excellent prospects for future use [11].

The aim of our investigation was to study the new catalytic organometallic compounds for epoxidation of vegetable oils. Epoxidation was carried out with two different types of catalytic systems (methyltrioxorhenium and peroxophosphatotungstate) and the merits of these systems are also discussed.

## Materials and Methods

### Chemicals

Soybean oils, sunflower oils, rapeseed oils, fatty acid methyl ester, cotton oils and palm oils were supplied by COFCO (China). MTO, tungstenic acid were obtained from Aldrich. Other reagents, including nitrogen donor ligands were purchased from commercial sources. All chemicals were used without further purification.

## Representative Procedure for the Preparation of Peroxophosphatotungstate Catalysts

### Synthesis of $[(C_4H_7)_4N]_3\{PO_4[WO(O_2)_2]_4\}$

A suspension of tungstic acid (2.50 g, 10 mmol) in 7 mL of 30% aqueous $H_2O_2$ was stirred and heated to 60 °C until a colorless solution was obtained. This solution was filtered, cooled to room temperature, and then 40% w/v $H_3PO_4$ (0.62 mL, 2.5 mmol) was added and the mixture was diluted to 30 mL with water. To the resultant solution, $[(C_4H_7)_4N]Br$ (5 mmol) in dichloromethane (40 mL) was added dropwise with stirring over about 2 min. Stirring was continued for an additional 15 min. The organic phase was then separated, dried over $Na_2SO_4$, filtered, and gently evaporated on a rotary evaporator under reduced pressure at 40–50 °C to give the solid catalyst. IR (neat, KBr plates) $cm^{-1}$: 2,721; 2,871; 2,923; 2,986; 1,472; 1,460; 1,405; 1,376; 1,366; 1,322; 1,310; 1,240; 1,163; 1,082 (P–O); 1,065; 1,031; 991; 970 (W=O); 921; 895; 885 ($W–O_b–W$); 863, 847 (O–O); 792; 736; 721; 589($W(O_b–O)$); 547 ($W(O)_2$); 540 ($W(O)_2$); 524 ($W(O_b–O)$).

### Synthesis of $[C_{16}H_{33}N(CH_3)_3]_3\{PO_4[WO(O_2)_2]_4\}$

IR (neat, KBr plates) $cm^{-1}$: 3,031; 3,015; 3,002; 2,965; 2,942; 2,915; 2,871; 2,858; 1,483; 1,480; 1,471; 1,460; 1,427; 1,405; 1,393; 1,381; 1,085 (P–O); 985; 982; 968 (W=O); 935; 910; 902; 885 ($W–O_b–W$), 845 (O–O); 728; 714; 593 ($W(O_b–O)$); 548 ($W(O)_2$); 540 ($W(O)_2$); 522 ($W(O_b–O)$).

### Synthesis of $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3\{PO_4[WO(O_2)_2]_4\}$

IR (neat, KBr plates) $cm^{-1}$: 3,420; 3,126; 3,044; 3,032; 2,918; 2,848; 1,630; 1,560; 1,555; 1,550; 1,500; 1,485; 1,465; 1,375; 1,312; 1,212; 1,171; 1078 (P–O); 946 (W=O); 884 ($W–O_b–W$); 682; 544 ($W(O)_2$).

### Synthesis of $[(C_{12}H_{25})_3NCH_3]_3\{PO_4[WO(O_2)_2]_4\}$

IR (neat, KBr plates) $cm^{-1}$: 3,462; 2,919; 2,850; 2,356; 1,733; 1,634; 1,476; 1,377; 1,080 (P–O), 941 (W=O); 884 ($W–O_b–W$); 831 (O–O); 721; 600 ($W(O_b–O)$); 542 $cm^{-1}$ ($W(O)_2$); 530 ($W(O_b–O)$).

### Synthesis of $[(C_{18}H_{37})_2N(CH_3)_2]_3\{PO_4[WO(O_2)_2]_4\}$

IR (neat, KBr plates) $cm^{-1}$: 3,540; 3,462; 3,413; 2,929; 2,840; 1,625; 1,476; 1,377; 1,103, 1,055, 1,003 (P–O); 947 (W=O); 887, 866 ($W–O_b–W$); 818 (O–O); 721; 592($W(O_b–O)$); 546 ($W(O)_2$); 526 ($W(O_b–O)$).

### Catalytic Experiments

Epoxidation with peroxophosphatotungstate: 20 g oils and 0.15 mmol catalyst were added in a 100-ml three-necked flask. The mixture was stirred and heated to the desired temperature. Then 10 g hydrogen peroxide was added portion wise for 2.5 h and stirred for some hours. After the reaction, the organic phase was separated and washed with ethyl ether. The solvent was removed on a rotary evaporator under a low vacuum to afford the epoxidized oils. The epoxidized oils were finally dried under vacuum.

Epoxidation with MTO: 30 g oils was dissolved in 30 mL $CH_2Cl_2$ followed by the addition of 3 mmol MTO, 0.15 mol adduct (nitrogen donor ligand such as pyridine) and $H_2O_2$ dropwise to the solution. The mixture was vigorously stirred at the desired temperature. After 4 h, a sodium bisulfite solution (20%, 0.1 mol) was added and the mixture stirred for 30 min. The organic phase was separated and washed with a 0.2-mol aqueous solution of tartaric acid (10%) to remove the adduct followed with an aqueous solution of $NaHCO_3$. Then it was filtered through an alumina basic column using a (1:1) mixture of hexane and ethyl acetate as eluent. The epoxidized oils were dried under vacuum.

All of the above reactions were performed at least three times, in independent experiments, and presented good reproducibility (error $< 5\%$).

Conversion: amount of double bonds converted.
Selectivity: amount of epoxide formed/amount of double bonds converted.

### Characterization Methods

IR analyses were performed on a Thermo NEXUS FT-IR Spectrometer. The $^1$H- and $^{13}$C-NMR spectra was acquired on an AVANCE III 400 MHz digital NMR spectrometer (Bruker, Germany) using $CDCl_3$ as a solvent, which contained 0.03% trimethylsilane (Nacalai Tesque Inc.), and the resulting solution was placed in a 5-mm NMR tube. The $^{31}$P-NMR solution spectra were obtained on an AVANCE III 400 MHz Digital NMR Spectrometer. One percent $H_3PO_4$ in $D_2O$ was used as an external reference. UV–Vis analyses were performed using a Shimadzu UV-240 UV/Vis spectrophotometer. The reaction conversion was monitored by the area decrease of the double-bond hydrogen signals [12].The presence of signals at 53.4 and 55.9 ppm in the $^{13}$C-NMR spectra was assigned to the epoxy carbons [13]. X-ray Diffraction analysis was performed on a Bruker Advance D8, and $2\theta$ is from 5 to 35°. For photoelectron excitation was used copper anode X-rays under tube voltage 30 kV and emission current 20 mA. TG analyses were performed on a NETZSCH STA-409.

## Results and Discussion

### Epoxidation by $H_2O_2$ Catalyzed by Peroxophosphatotungstate

The effect of different peroxophosphatotungstates on the oils conversion and product selectivity are given in Table 1 for the comparative purpose. $[(C_{18}H_{37})_2N(CH_3)_2]_3\{PO_4[WO(O_2)_2]_4\}$ has best catalytic properties on the epoxidation of vegetable oil among these prepared catalysts. Because $\{PO_4[WO(O_2)_2]_4\}^{3-}$ is soft base, it is inclined to react with soft acids. As the $[(C_4H_9)_4N]^+$ is hard acid with higher charge density, it is easier to react with hard ion $OH^-$. It is more difficult to react with the $\{PO_4[WO(O_2)_2]_4\}^{3-}$. While $[(C_{18}H_{37})_2N(CH_3)_2]^+$ is the soft acid, which is apt to form ion pairs with $\{PO_4[WO(O_2)_2]_4\}^{3-}$ to achieve phase transfer catalytic process.

**Table 1** Influence of the catalyst on the epoxidation

| Catalysts | Conversion (%) | Selectivity (%) |
|---|---|---|
| $H_3PO_4 + H_2WO_4$ | 23.1 | 0 |
| $[(C_4H_9)_4N]_3\{PO_4[WO(O_2)_2]_4\}$ | 24.5 | 0 |
| $[(C_{16}H_{33})N(CH_3)_3]_3\{PO_4[WO(O_2)_2]_4\}$ | 38.5 | 3.84 |
| $[(\pi\text{-}C_5H_5)NC_{16}H_{33}]_3\{PO_4[WO(O_2)_2]_4\}$ | 42.3 | 7.4 |
| $[(C_{12}H_{25})_3NCH_3]_3\{PO_4[WO(O_2)_2]_4\}$ | 82.1 | 80.1 |
| $[(C_{18}H_{37})_2N(CH_3)_2]_3\{PO_4[WO(O_2)_2]_4\}$ | 86.2 | 83.8 |

20 g soybean oil (0.10 mol double bond), 0.15 mmol catalyst, 10 g (0.10 mol) 35% $H_2O_2$, temperature: 60 °C, time: 4 h. The errors of the reaction are below 5%

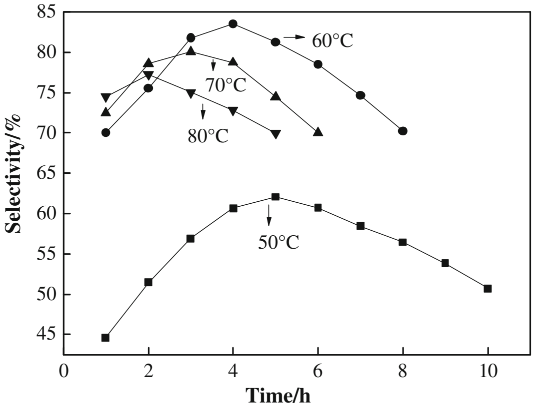

**Fig. 1** Effect of reaction time and temperature on epoxidation of soybean oils[a]. [a]20 g soybean oil (0.10 mol double bond), 0.15 mmol $[(C_{18}H_{37})_2N(CH_3)_2]_3\{PO_4[WO(O_2)_2]_4\}$, 10 g (0.10 mol) 35% $H_2O_2$. The errors of the reaction are below 5%

The effects of reaction temperature and time are shown in Fig. 1. The reaction rate is influenced by temperature as the solubility of peroxophosphatotungstate in the soybean oil is affected by temperature. The catalytic perspective is enhanced as the temperature rose (Fig. 1). Raising the temperature was found beneficial for increasing the selectivity of epoxidation. Nevertheless, when the temperature exceeded 60 °C, hydrogen peroxide decomposition reaction and ring-opening of the epoxide ring were accelerated. As a result, the conversion and selectivity of epoxidation declined.

At the beginning of the reaction, the selectivity of epoxidation increased along with time. However, selectivity of the reaction was reduced as the reaction time was further increased. The rate of the epoxidation catalyzed by peroxophosphatotungstate is low and the amount of hydrogen peroxide (relative to the double bond of the soybean oil) is excessive, so that the ring-open reaction caused the selectivity of epoxidation to decrease.

### Characterization of $[(C_{18}H_{37})_2N(CH_3)_2]_3\{PO_4[WO(O_2)_2]_4\}$

$[(C_{18}H_{37})_2N(CH_3)_2]_3\{PO_4[WO(O_2)_2]_4\}$ is the best catalyst used for epoxidation (Table 1). So we focused on the characterization of $[(C_{18}H_{37})_2N(CH_3)_2]_3\{PO_4[WO(O_2)_2]_4\}$.

Figure 2 shows the $^{31}$P-NMR spectrum of $[(C_{18}H_{37})_2N(CH_3)_2]_3\{PO_4[WO(O_2)_2]_4\}$ in $CDCl_3$. It had no peak near −14.68 ppm, which is attributed to $[PW_{12}O_{40}]^{3-}$ [14] and contains the signal at 1.46 ppm assigned to $\{PO_4[WO(O_2)_2]_4\}^{3-}$ [15] and other unidentified signals at −8.64, −7.89, −7.54, 9.94 and 10 ppm probably from peroxo polyanions $PW_xO_y^{z-}$ ($x = 1$–4), containing diperoxo units

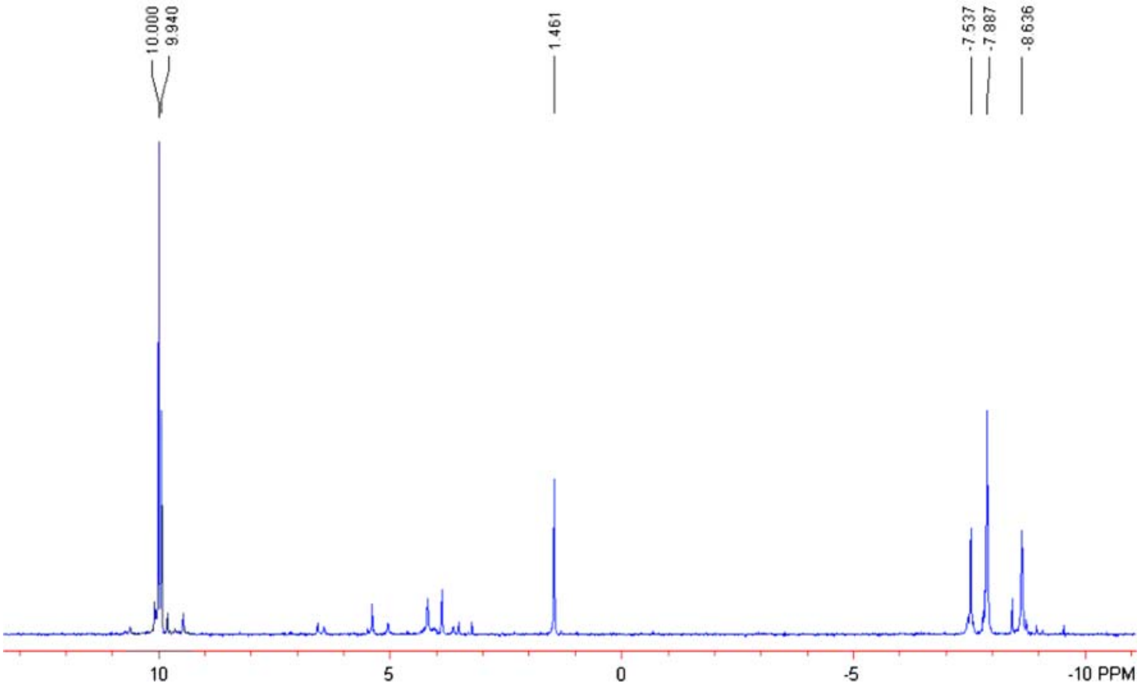

**Fig. 2** $^{31}$P-NMR spectrum of a solution of $[(C_{18}H_{37})_2N(CH_3)_2]_3\{PO_4[WO(O_2)_2]_4\}$

$WO(O_2)_2$ [16]. And it has been shown that $WO(O_2)_2$ in the peroxo polyanions $PW_xO_y^{Z-}$ are labile [17], so peroxo phosphotungstic species present in the system are likely to exist in the fast equilibrium. It indicates that $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and other peroxo polyanions $PW_xO_y^{z-}$ may play an active role in the epoxidation.

UV–Vis experiments were used to observe the reaction: two absorption bands of the catalyst were obtained (Fig. 3): One was sharp absorption near 207 nm which was assigned to the terminal oxygen to tungsten ($O_d \rightarrow W$) charge transfer absorption band. Another absorption band at 264 nm was assigned to ligand ($O_b$, $O_c$) to the metal (W) charge transfer which was the characteristic band of the polyanionic structure. After the reaction, the absorption band at 264 nm appeared which proved the catalyst (peroxophosphatotungstate) had donated the oxygen atom to the double bonds of the oils and generated the phosphatotungstate.

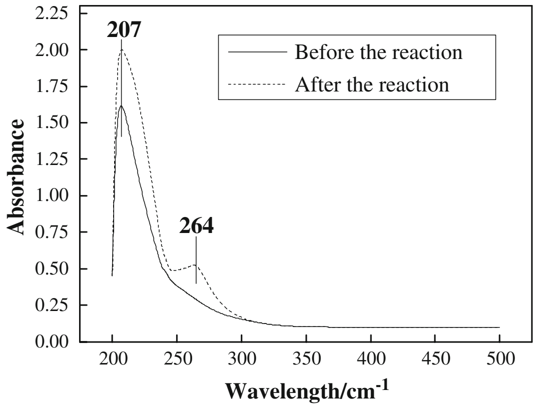

**Fig. 3** UV–Vis spectrum characters of catalyst during epoxidation[a]. [a]20 g soybean oil (0.10 mol double bond), 0.15 mmol $[(C_{18}H_{37})_2N(CH_3)_2]_3\{PO_4[WO(O_2)_2]_4\}$, 10 g (0.10 mol) 35% $H_2O_2$, temperature: 60 °C, time: 4 h

The location of diffracted ray depends on the lattice structure in the crystal, and diffracted intensity lies on the atom site in the crystal cell. In the reaction of $H_3PW_{12}O_{40}$ with hydrogen peroxide, $\{PO_4[WO(O_2)_2]_4\}^{3-}$ is contained in the decomposition product. The characteristic diffraction peak of Keggin heteropoly acid appears in the areas of $2\theta$ from 7 to 10° and 19–25° (Fig. 4). It proves product obtained from the heteropoly negative ion reacts with quaternary ammonium salt retains the configuration of

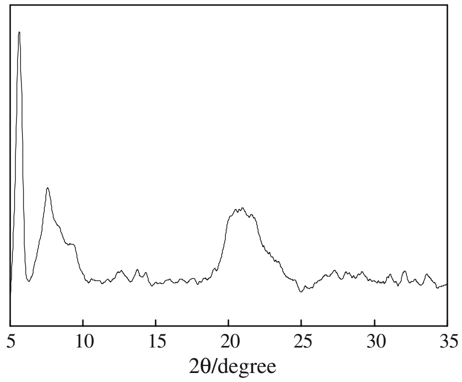

**Fig. 4** X-ray pattern of $[(C_{18}H_{37})_2N(CH_3)_2]_3\{PO_4[WO(O_2)_2]_4\}$

Keggin heteropoly acid. While there is a sharp diffraction peak the range of $2\theta$ indicating that the configuration of peroxoheteropoly acid is different from the Keggin heteropoly acid.

When examined by TG, $[(C_{18}H_{37})_2N(CH_3)_2]_3\{PO_4[WO(O_2)_2]_4\}$ decomposed and lost weight as the temperature was raised. This process is divided into two stages (Fig. 5). The boundaries of the first one (1) are from 50 to 400 °C, the catalyst decomposed relatively slowly during this stage, due to quaternary ammonium salt positive ion decomposing to quaternary ammonium salt positive ion of simple long chain. Weight loss ratio is 60.3%, the same as the theoretical value. And the second one (2) is from 400 to 480 °C, as the negative ion in the catalyst decomposed partly and generated $P_2O_5$. When the temperature rose over 480 °C, the rest of catalyst became more stable and decomposition stopped. The weight-loss ratio of catalyst at 100 °C is less than 2%, which indicates the catalyst in the low-temperature environment is comparatively stable.

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When examined by TG, $[(\pi\text{-}C_5H_5)NC_{16}H_{33}]_3\{PO_4[WO(O_2)_2]_4\}$ decomposed and lost weight as the temperature rose. This process is divided into two stages (Fig. 5). The boundaries of the first one (1) are from 50 to 500 °C, the catalyst decomposed relatively slowly in this stage, due to the quaternary ammonium salt positive ion decomposing to the quaternary ammonium salt positive ion of simple long chain. Weight loss ratio is 52.7%, same as the theoretical value. And the second one (2) is from 500 to 600 °C, when the temperature reached 500 °C. As the negative ion in the catalyst decomposed partly and generated $P_2O_5$. When the temperature rose to over 600 °C, the rest of catalyst became more stable and decomposition stopped. The weight-loss ratio of catalyst at 100 °C is less than 2%, which indicates the catalyst in the low-temperature environment is comparatively stable.

## Epoxidation of the Soybean Oil by $H_2O_2$ Catalyzed by MTO

We investigated the effect of reaction temperature on the epoxidation of soybean oil. Figure 6 shows the conversion and selectivity at different temperatures and MTO/double bond molar ratio is 0.01. At low temperature (0 °C), the selectivity of epoxidation is comparatively low. As the reaction at low temperature processed for a long time which makes the oxirane ring hydrolyze. With increasing reaction temperature (from 0 to 20 °C), the conversion and selectivity for epoxide increased. The selectivity keeps nearly constant in the reaction temperature range form 20–40 °C, whereas the conversion increased with increasing temperature.

Table 2 depicts the effect of MTO concentration on the level of soybean oils epoxidation. An increase in the MTO concentration (with respect to the double bond of oils) resulted in an increase in the soybean oils conversion initially before leveling off at 95.45%. Epoxidized oils selectivity gradually increases from a comparatively lower

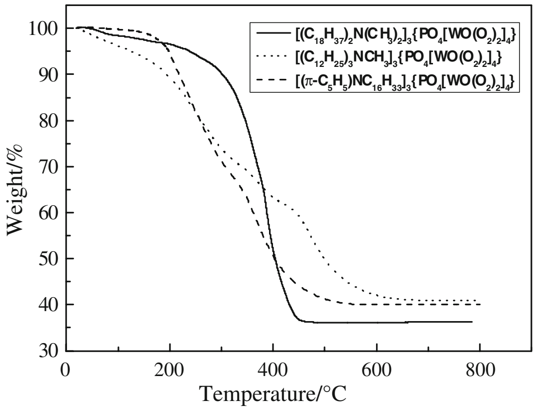

**Fig. 5** TG chart of catalyst[a]. [a]Air velocity: 20 ml/min, temperature rate: 15 °C/min, range of temperature: 20–800 °C

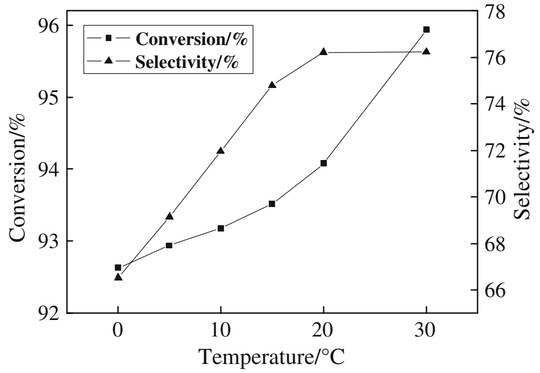

**Fig. 6** Influence of reaction temperature on the epoxidation reaction[a]. [a]10 g soybean oil (51.2 mmol double bond), n(MTO):n($H_2O_2$):n(double bond) = 1:200:100, solvent: 30 mL $CH_2Cl_2$. The errors of the reaction are below 5%

**Table 2** Influence of dosage of catalyst on the epoxidation reaction

| No | n(MTO): n(double bond) | Time (h) | Conversion (%) | Selectivity (%) |
|---|---|---|---|---|
| 1 | 1:100 | 4 | 95.49 | 76.22 |
| 2 | 0:100 | 16 | 38.37 | 48.50 |
| 3 | 1:400 | 16 | 94.83 | 52.85 |
| 4 | 1:300 | 14 | 95.20 | 56.12 |
| 5 | 1:200 | 12 | 95.41 | 68.09 |
| 6 | 1:150 | 8 | 95.45 | 72.67 |
| 7 | 1:50 | 3 | 95.45 | 76.14 |

10 g soybean oil (51.2 mmol double bond), n($H_2O_2$):n(double bond) = 2:1, solvent: 30 mL $CH_2Cl_2$, temperature: 20 °C. The errors of the reaction were below 5%

value of 52.85% to the maximum value of 76.18% with increasing catalyst concentration.

The catalytic system first reacts with $H_2O_2$ to form reactive intermediate (peroxorhenium complexes). Then the formed intermediate attacks the double bond in the oils. The selectivity of the epoxidation with high mass fraction of hydrogen peroxide is relatively high (Table 3). A high mass fraction of hydrogen peroxide can reduce the pH of the catalytic system and increase the Lewis acidity of the rhenium center. And it results in the formation of 1,2-diols from epoxidized products. Furthermore, the high mass fraction of hydrogen peroxide in the system may cleave the double bonds to generate byproducts such as ketone and so on. This indirectly indicates the main function of hydrogen peroxide in the epoxidation is coordination instead of oxidizability.

The selectivity and conversion of the epoxidation increased along with the increase in the hydrogen peroxide content of the reaction mixture. When n ($H_2O_2$): n (double bond) reaches 2.5:1, the optimum levels of epoxidation could be attained.

**Table 3** Influence of $H_2O_2$ on the epoxidation reaction

| No | w($H_2O_2$)/% | pH[a] | n($H_2O_2$): n(double bond) | Conversion (%) | Selectivity (%) |
|---|---|---|---|---|---|
| 1 | 10 | 5.32 | 2:1 | 95.49 | 76.22 |
| 2 | 30 | 4.74 | 2:1 | 95.58 | 71.30 |
| 3 | 50 | 4.52 | 2:1 | 95.75 | 71.50 |
| 4 | 10 | 5.32 | 1:1 | 94.74 | 65.73 |
| 5 | 10 | 5.32 | 1.5:1 | 95.14 | 71.44 |
| 6 | 10 | 5.32 | 2.5:1 | 95.62 | 78.54 |
| 7 | 10 | 5.32 | 3:1 | 95.63 | 78.60 |
| 8 | 10 | 5.32 | 4:1 | 95.62 | 78.58 |

10 g soybean oil (51.2 mmol double bond), n(MTO):n($H_2O_2$):n(double bond) = 1:200:100, no adduct, solvent: 30 mL $CH_2Cl_2$. The errors of the reaction were below 5%

[a] The value of pH was evaluated by using an acidometer

**Table 4** Influence of solvents on the epoxidation reaction

| No | Solvents | Dielectric constant (ε)[a] | Conversion (%) | Selectivity (%) |
|---|---|---|---|---|
| 1 | $CH_3CN$ | 36.64 | 95.78 | 82.62 |
| 2 | $CH_3OH$ | 33.0 | 87.83 | 60.84 |
| 3 | $CH_3COCH_3$ | 21.01 | 91.84 | 75.51 |
| 4 | $ClCH_2Cl$ | 8.93 | 88.78 | 62.86 |
| 5 | $CHCl_3$ | 4.8069 | 85.24 | 58.74 |
| 6 | $CH_3Ph$ | 2.379 | 80.34 | 55.42 |

10 g soybean oil (51.2 mmol double bond), n(MTO):n($H_2O_2$):n(double bond) = 1:200:100, 30 mL solvent, temperature: 20 °C, time: 4 h. The errors of the reaction were below 5%

[a] Data of ε are from ref. [20]

Table 4 shows the catalytic system is influenced by the species of solvent. Reactivity of the catalytic system is highest when acetonitrile was used as the solvent. The selectivity of the reaction when aprotic solvents such as acetone, acetonitrile were used as solvent is higher than that of the protic solvent methanol. This is because the solubility of catalytically active peroxorhenium complexes is higher in aprotic solvents (ether, acetonitrile) relative to the protic solvent (methanol). The selectivity of epoxidation in the aprotic solvent increased as the dielectric constant of the solvent increased. Solvent effect in catalysis has been reported in the literature [18, 19]. In this case, the solvent effect can be explained in the following manner: $H_2O_2$ exists in equilibrium with $HO_2^-$ and $H^+$, and the existence of these ions as an ion pair or as free ions will be defined by the dielectric constant of the solvent. The solvent with the higher dielectric constant will more readily accommodate the existence of free ions, resulting in a much more active system than that with lower dielectric constant.

Methyltrioxorhenium acted as an efficient catalyst for the olefin epoxidation. However, the most important drawback of the MTO-catalyzed process is the concomitant formation of 1,2-diols instead of the desired epoxides. So we observed the influence of adduct on the epoxidation reaction (Fig. 5) and the results are presented in Table 5.

Value of the equilibrium constants have been evaluated for the reactions by the chemical equation:

$$\mathrm{MTO} + L = \mathrm{MTO}\cdot LK = \frac{[\mathrm{MTO}\cdot \mathrm{L}]}{[\mathrm{MTO}][L]} \qquad (1)$$

The absorbance of a solution at equilibrium is sum of the larger component from the adduct of $\mathrm{MTO{\cdot}L}$ and the smaller one from MTO:

$$\text{Absorbance} = \varepsilon_{\mathrm{MTO}}[\mathrm{MTO}] + \varepsilon_{\mathrm{MTO-L}}[\mathrm{MTO.L}] \qquad (2)$$

The mass balance for rhenium must also be maintained:

$$[\mathrm{MTO}]_0 = [\mathrm{MTO}] + [\mathrm{MTO.L}] \qquad (3)$$

**Table 5** Influence of adduct on the epoxidation reaction

| No | Amine adduct | pK$_a^a$ | Selectivity (%) | Conversion (%) |
|---|---|---|---|---|
| 1 | None | – | 82.62 | 95.78 |
| 2 | Pyridine | 5.23 | 99.40 | 99.83 |
| 3 | Imidazole | 6.99 | 99.50 | 99.91 |
| 4 | Pyrazole | 2.49 | 94.58 | 97.34 |
| 5 | Thiazole | 2.52 | 94.62 | 97.36 |
| 6 | Pyrrole | −3.8 | 83.75 | 95.97 |
| 7 | 3-Cyanopyridine | 1.78 | 89.46 | 96.24 |
| 8 | 3-Bromopyridine | 2.87 | 94.96 | 97.82 |
| 9 | 3-Choropyridine | 2.95 | 95.02 | 97.94 |
| 10 | Pyridine-4-aldehyde | 3.30 | 95.36 | 98.18 |
| 11 | 3-Phenylpyridine | 4.85 | 95.64 | 98.26 |
| 12 | 3-Methylpyridine | 5.52 | 99.46 | 99.88 |
| 13 | 4-Methylpyridine | 5.94 | 99.48 | 99.84 |
| 14 | 2-Choropyridine | 0.62 | 84.68 | 96.02 |
| 15 | 2,6-Dimethylpyridine | 6.67 | 86.28 | 96.12 |
| 16 | 2,6-Di-*tert*-butyl-4-methylpyridine | 6.68 | 85.46 | 96.08 |

10 g soybean oil (51.2 mmol double bond), solvent: 30 mL $CH_2Cl_2$, temperature: 20 °C, time: 2 h, n(adduct):n(MTO):n($H_2O_2$):n(double bond) = 50:1:250:100. The errors of the reaction were below 5%

[a] Data of *K* are from ref. [20]

The simultaneous solution of these equations, which is presented in the supporting information, affords an exact expression for the equilibrium absorbance in which the indicated equilibrium is sustained:

$$\text{Absorbance} = \frac{\varepsilon_{\text{MTO}} + \varepsilon_{\text{MTO}-L}K[L]}{1 + K[L]}[\text{MTO}]_0 \tag{4}$$

Here [*L*] represents the equilibrium ligand concentration. The values of *K* were determined for most of ligands by citing the equilibrium absorbances to Eq. 4.

$$\text{Absorbance} \times (1 + K[L]) = [\text{MTO}]_0 \times (\varepsilon_{\text{MTO}} + \varepsilon_{\text{MTO}-L}K[L]) \tag{5}$$

$$K[L] = \frac{A_x - A_0}{A_\infty - A_x} \tag{6}$$

$$\log K + \log[L] = \log\left[\frac{A_x - A_0}{A_\infty - A_x}\right] \tag{7}$$

The data were subsequently analyzed by plotting $\log[(A_x - A_0)/(A_\infty - A_x)]$ versus $\log[L]$ (where $A_0$ and $A_\infty$ represent the absorbance at 0 and 100% formation of MTO.L, respectively, and $A_x$ is the absorbance at any given *L* concentration, [*L*]) which resulted in a good linear plot with a slope of ≈1.00, indicating the only one pyridine is coordinated to MTO (Figs. 7, 8). The intercept of this linear plot gives the value of log *K*, which is in excellent agreement with the directly determined value described above. We obtained similar fitting curves for several adducts, and the results are summarized in Table 6.

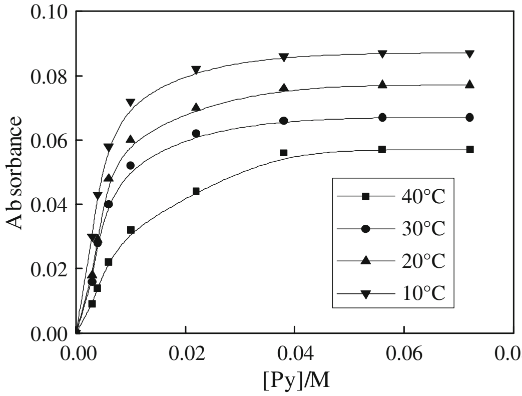

**Fig. 7** Changes in absorbance at 360 nm on addition of pyridine to MTO in ethyl acetate at different temperatures

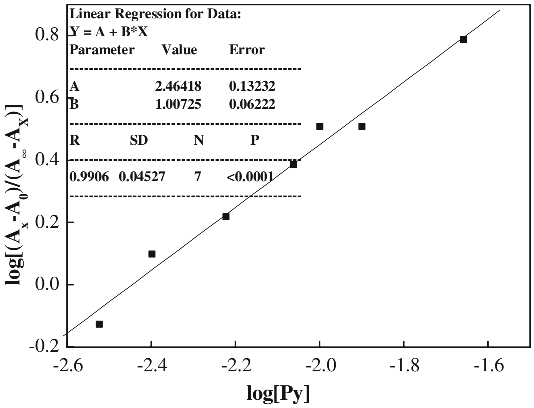

**Fig. 8** Plot of log $[(A_x - A_0)/(A_\infty - A_x)]$ vs log[Py] Solvent: $CH_2Cl_2$, $T = 20$ °C

The selectivity of epoxidation increased as the pK of formation of ligands increased. While the selectivity of no 15 and 16 (Table 5) is low, because their relatively lower pK (Table 6) makes adduct's ability of electron donating reduced.

## Characterization of MTO

Figure 9 shows ($Et_2O$, 20 °C): The MTO has no sharp absorption from 300 to 500 nm. But when $H_2O_2$ was added to the MTO, the sharp absorption at 365 nm appeared, which is assigned to the oxygen to rhenium ($O_2$ → Re) charge transfer absorption band. And this proves $(CH_3)Re(O_2)_2O{\cdot}H_2O$ is generated during the process.

The mechanism of epoxidation catalyzed by organometallic compounds depends upon the interactions that occur between the unsaturated long-chain organic compounds HOMO π(C–C) and the unoccupied peroxo

**Table 6** Formation constants (L mol$^{-1}$) for the coordination of adduct to MTO

| No | Ligand | $K$ (L mol$^{-1}$) |
|---|---|---|
| 1 | Pyridine | 185.2 ± 21.0 |
| 2 | Imidazole | 697.9 ± 38.7 |
| 3 | Pyrazole | 25.86 ± 1.8 |
| 4 | Thiazole | 23.44 ± 0.6 |
| 5 | Pyrrole | 0.84 ± 0.4 |
| 6 | 3-Cyanopyridine | 7.21 ± 0.14 |
| 7 | 3-Bromopyridine | 23.3 ± 0.2 |
| 8 | 3-Choropyridine | 21.8 ± 0.3 |
| 9 | Pyridine-4-aldehyde | 36.8 ± 0.9 |
| 10 | 3-Phenylpyridine | 156 ± 4 |
| 11 | 3-Methylpyridine | 254 ± 11 |
| 12 | 4-Methylpyridine | 732 ± 20 |
| 13 | 2-Choropyridine | <1 |
| 14 | 2,6-Dimethylpyridine | <1 |
| 15 | 2,6-Di-*tert*-butyl-4-methylpyridine | <1 |

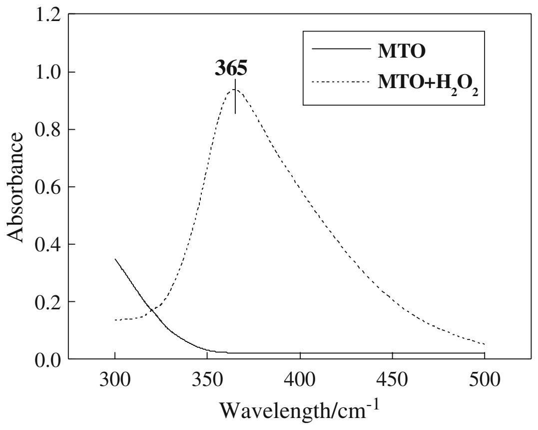

**Fig. 9** UV/Vis spectra of rhenium catalytic system

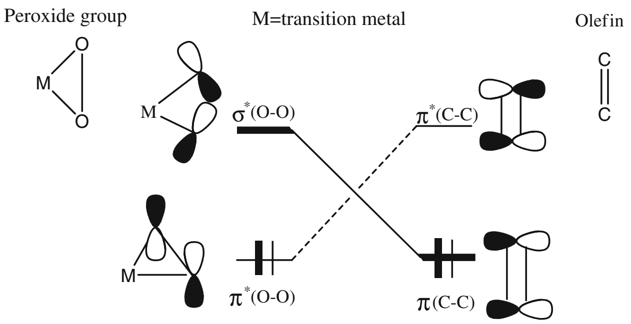

**Fig. 10** Frontier orbital interaction between a transition metal peroxo group and an olefin

$\sigma^*$(O–O) orbital, which is among the LUMO group of the metal peroxo complex (Fig. 10). As the peroxo group, formally an $O_2^{2-}$ ligand interacts with the metal center via donation from its orbital to formally empty *d* orbital of the metal center. The highest occupied orbital of the peroxo group ($\pi^*$(O–O)) is strongly involved in the interaction with the empty *d* orbital of the metal center. This reduces the O–O antibonding character of $\pi^*$orbital and leads to a strengthening of the O–O bond. So O–O bond in the $\pi^*$(O–O) orbital is difficult to break through. And electron density is redistributed from the C–C bonding unsaturated long-chain organic compounds orbital to an O–O antibonding orbital, which entails O–O bond activation. As a result, these kinds of catalyst are active in the epoxidation.

As soybean oil is typical oil, and the epoxidation of it proceeds smoothly. Then fatty acid methyl ester, sunflower oil, rapeseed oil, cottonseed oil and palm oil were selected to test this catalytic system, and the reaction results are listed in Table 7. The data in the experiment shows selectivity of epoxidized product could reach above 99%, which indicates catalytic system is very active in epoxidation of long-chain unsaturated compounds.

The epoxidation of the oils catalyzed by two kinds of compounds (methyltrioxorhenium and peroxophosphatotungstate) was studied. The results are summarized as follows: (1) The organic peracid generated in the process is very unstable and is liable to cause explosion. And the equipment is corroded severely, the selectivity is low. The stability of the product is comparatively poor. Above all, a large number of the waste water -carboxylic acid is generated in the process leading to serious environmental pollution. (2) The reaction catalyzed by the organometallic compounds involves no carboxylic acid to achieve “zero release”. So this can be desirable for an environmentally benign chemistry. And this kind of catalytic system has been proved to be extremely efficient (in both activity and selectivity) for the epoxidation of vegetable oils. And the only by-product is water. At the same time, the condition of reaction is mild. These advantages of the organometallic compounds suggest that it would be used as a green alternative of catalysts for the epoxidation of long-chain unsaturated compounds.

The epoxidation catalyzed by organometallic compounds is a novel process, in which it is believed that the reactions are mediated by a group of the metal peroxo complexes [21]. Because vegetable oils are typical long-chain unsaturated compounds, it may provide new routes for preparing other long-chain epoxidized compounds.

**Table 7** Catalyst applied in the epoxidation of other oils

| No | Oils | MTO[a] | | Peroxophosphatotungstate[b] | |
|---|---|---|---|---|---|
| | | Selectivity (%) | Yield (%) | Selectivity (%) | Yield (%) |
| 1 | Fatty acid methyl ester | 99.36 | 99.14 | 98.56 | 97.55 |
| 2 | Sunflower oil | 99.28 | 98.96 | 98.42 | 97.26 |
| 3 | Rapeseed oil | 99.24 | 98.86 | 98.38 | 97.16 |
| 4 | Cottonseed oil | 99.16 | 98.70 | 98.24 | 96.88 |
| 5 | Palm oil | 99.12 | 98.54 | 98.20 | 96.72 |
| 6 | Soybean oil | 99.90 | 99.80 | 98.86 | 98.76 |

[a] Solvent: 30 mL $CH_3CN$, n(imidazole):n(MTO):n($H_2O_2$):n(double bond) = 50:1:250:100, temperature: 20 °C, time: 2 h. The errors of the reaction were below 5%

[b] 20 g oil (0.10 mol double bond), 0.15 mmol $[(C_{18}H_{37})_2N(CH_3)_2]_3\{PO_4[WO(O_2)_2]_4\}$, 10 g (0.10 mol) 35% $H_2O_2$, temperature: 60 °C, time: 4 h. The errors of the reaction were below 5%

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