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# A spectroscopic study on the 12-heteropolyacids of molybdenum and tungsten ($H_3PMo_{12-n}W_nO_{40}$) combined with cetylpyridinium bromide in the epoxidation of cyclopentene

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**Abstract**

The epoxidation of cyclopentene with hydrogen peroxide catalyzed by 12-heteropolyacids of molybdenum and tungsten ($H_3PMo_{12-n}W_nO_{40}$, $n = 1$–11), 12-tungstophosphoric acid and 12-molybdophosphoric acid combined with cetylpyridinium bromide as a phase transfer reagent was carried out in acetonitrile. Among 13 heteropolyacids investigated, catalyst of $H_3PMo_6W_6O_{40}$ showed the highest activity, giving a conversion of 60% and a selectivity of 95% in the epoxidation of cyclopentene. The fresh catalysts and the catalysts under reaction condition were characterized by UV–vis, FT-IR and $^{31}P$ NMR spectroscopy, which has revealed that all of the molybdotungstophosphoric acids were degraded in the presence of hydrogen peroxide to form a considerable amount of phosphorus-containing species. The active species resulted from $H_3PMo_6W_6O_{40}$ are new kinds of phosphorus-containing species, which is different from $\{PO_4[WO(O_2)_2]_4\}^{3-}$.


*Keywords:* Molybdotungstophosphoric acids; Cyclopentene; Hydrogen peroxide; PMW/CPB; $PW_{12}$/CPB

## 1. Introduction

Epoxidation of alkenes is among the most important reactions in organic synthesis, because epoxide compounds are valuable precursors for the synthesis of drugs, agrochemicals and food additives. Polyoxometalates, as the effective catalysts for epoxidation, have drawn wide attention in the last two decades [1–24]. In 1983, Venturello et al. [7–9] discovered that the complex consisting of tungstate and phosphate can catalyze the epoxidation of different alkenes with dilute $H_2O_2$ solution (15%) as oxidant. In 1988, Ishii and co-workers [10,11] reported that the system composed of $H_3PW_{12}O_{40}$ and cetylpyridinium chloride can catalyze epoxidation of alkenes with commercially available $H_2O_2$ solution (35%) as oxidant. In recent years, the epoxidation mechanism on these catalysts has been investigated by many groups [12–17]. It has been proved that $\{PO_4[WO(O_2)_2]_4\}^{3-}$ is the active species in the olefin epoxidation in the Venturello–Ishii system. Heteropolyacids with the Keggin structure, $H_3PW_{12}O_{40}$, are degraded in the presence of excess $H_2O_2$ to form peroxo species $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$, which are the true catalytic-active intermediate.

When we used $H_3PMo_{12-n}W_nO_{40}$ combined with cetylpyridinium bromide (abbreviated CPB) as a phase transfer reagent with 50 equiv of $H_2O_2$ solution (30%) to catalyze epoxidation of cyclopentene in acetonitrile, we found a new phenomenon. The epoxidation was more efficiently catalyzed by $H_3PMo_6W_6O_{40}$ combined with CPB (abbreviated as PMW/CPB system) than by $H_3PW_{12}O_{40}$ combined with CPB (abbreviated as $PW_{12}$/CPB system). At first sight,

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the poor reactivity of the $PW_{12}$/CPB system compared with the PMW/CPB system is difficult to understand. It seems that more active species resulted from $H_3PW_{12}O_{40}$ than from $H_3PMo_6W_6O_{40}$. In an attempt to interpret these results, we characterized the fresh catalysts and the catalysts under reaction condition by UV–vis, FT-IR and $^{31}$P NMR spectroscopy. It was found that the Keggin-type $H_3PMo_6W_6O_{40}$ is degraded completely in the presence of 50 equiv of $H_2O_2$ to form a considerable amount of phosphorus-containing species. Under the same reaction conditions, $H_3PW_{12}O_{40}$ is hardly degraded and no $\{PO_4[WO(O_2)_2]_4\}^{3-}$ is detected by $^{31}$P NMR.

## 2. Experimental

### 2.1. Preparation of heteropolyacids

All solvent and chemicals were analytical grade, commercially available and used without further purification unless otherwise stated.

$H_3PW_{12}O_{40}\cdot nH_2O$ was prepared according to Ref. [19]. $Na_2WO_4\cdot 2H_2O$ (25 g) and $Na_2HPO_4\cdot 12H_2O$ (10 g) were added to 40 ml of decationized water, and the mixture was refluxed at 80 °C with stirring. Then, 24% HCl (37.5 ml) was added to the solution at 80 °C. After the solution was concentrated to a volume of 25 ml by evaporation at 50 °C, it was cooled to room temperature. $H_3PW_{12}O_{40}$ was extracted with an equal amount of diethyl ether (with slow agitation after the addition of several drops of 37% HCl). Ether was removed at 50 °C. Then the residual was dissolved in water and concentrated at 50 °C. Recrystallization from an aqueous solution and drying in a desiccator for 2 d formed $H_3PW_{12}O_{40}\cdot nH_2O$.

$H_3PMo_{12}O_{40}\cdot nH_2O$ was prepared according to Ref. [20]. $MoO_3$ of 14.4 g was placed in a 250 ml flask equipped with a reflux condenser, and 140 ml of water was added. To this was then added 0.96 g of 85% $H_3PO_4$, and the solution was boiled for 3 h under vigorous stirring. The green color that developed was removed by the addition of a few drops of bromine water. At the end of the heating period, the yellow solution was cooled and the white insolubles remaining were filtered. The mother liquor was concentrated to a volume of 10 ml by evaporative boiling for 3–4 h. Upon cooling, the concentrate mixture was filtered and air-dried. This crude product was purified by dissolving in 10 ml of water, and was allowed the clear yellow solution to crystallize in air. The large yellow crystals formed were filtered and air-dried.

$H_3PMo_6W_6O_{40}\cdot nH_2O$ was prepared as follows [19]. $Na_2WO_4\cdot 2H_2O$ (15.0 g), $Na_2MoO_4\cdot 2H_2O$ (11.0 g) and $NaH_2PO_4\cdot 2H_2O$ (2.38 g) were dissolved in 66.7 ml of decatioinized water. The solution was kept at 80 °C for 3 h with agitation and then concentrated to 27 ml by evaporation. Then, 33.3 ml of 24% HCl was added (the solution was yellow). After extraction with ether at room temperature, crystals were obtained. Anal. found: P:Mo:W = 1.1:6:6.6, Calc. for $H_3PMo_6W_6O_{40}$: P:Mo:W = 1:6:6; yield: 57.7%.

Other $H_3PMo_{12-n}W_nO_{40}\cdot nH_2O$ heteropolyacids were similarly prepared.

### 2.2. Synthesis of peroxo complexes

#### 2.2.1. Preparation of $(CTP)_3\{PO_4[WO(O_2)_2]_4\}$

This was based on the method described by Ishii et al. [10]. To a solution of cetylpyridinium chloride (0.55 g, 1.55 mmol) in 35% $H_2O_2$ (20 ml) was added $H_3PW_{12}O_{40}$ (1.5 g, 0.55 mmol) in 35% $H_2O_2$ (5 ml), and the mixture was stirred at 40 °C for 4.5 h. The suspended mixture was cooled to room temperature until a white precipitate was produced. After centrifugation, the precipitate was washed repeatedly with water and dried in vacuum. IR (KBr): 3431, 2918, 2850, 1708, 1633, 1486, 1468, 1374, 1175, 1132, 1080, 1057, 982, 906, 836, 771, 721, 682, 648, 571, 548, and 525 $cm^{-1}$.

#### 2.2.2. Preparation of $(Bu_4N)_3\{PO_4[MoO(O_2)_2]_4\}$

This was based on the method described by Aubry [13]. 30% $H_2O_2$ (15 ml, 150 mmol) was added to a solution of $H_3PMo_{12}O_{40}$ (1.91 g, 1 mmol in 5 ml of water). After a few minutes of stirring, an insoluble fraction was removed by filtration. The clear yellow solution was left to stand for 15 min before an aqueous solution of tetrabutylammonium bromide (0.903 g, 2.8 mmol) was slowly added. The resulting yellow precipitate was filtered out, washed thoroughly with water, and air-dried. IR (KBr): 1071, 1039, 964, 872, 739, 660,590, 543, and520 $cm^{-1}$.

### 2.3. Catalytic reactions

The catalytic reactions were performed in a 10 ml two-necked round-bottomed flask equipped with a septum, a magnetic stirring bar, and a reflux condenser. Typically, cyclopentene (3 mmol) and 0.52 mmol of *n*-butyl ether as an internal standard were added to an acetonitrile solution (3 ml) of catalyst (0.015 mmol), cetylpyridinium bromide (0.045 mmol) and 30% hydrogen peroxide (0.75 mmol). The flask was then placed in a hot oil bath at 60 °C and the mixture was stirred vigorously for 3.5 h. The reaction solution was periodically sampled by a syringe and analyzed by a Perkin-Elmer XL gas chromatograph equipped with a 15 m SE-54 capillary column and a FID detector. Assignments of products were made by comparison with authentic samples. Selected samples were also analyzed by GC/MC (Agilent-6890/5973N).

### 2.4. UV–vis measurement

#### 2.4.1. UV–vis spectra were recorded on a Shimadzu UV-spectrometer

Samples without $H_2O_2$ added were treated as follows: heteropolyacid (0.015 mmol) and cetylpyridinium bromide (0.045 mmol) (abbreviated as the HPA/CPB system) were dissolved in acetonitrile (3 ml), and the UV spectra of these samples were recorded after 1 h.

Samples with $H_2O_2$ added were treated as follows: heteropolyacid (0.015 mmol) and cetylpyridinium bromide (0.045 mmol) were dissolved in 3 ml of acetonitrile, and then $H_2O_2$ (0.75 mmol) was added with stirring. The UV spectra of these samples were recorded after 1 h.

### 2.5. FT-IR spectra

IR spectra were recorded on a Nicolet AVATAR 360 FT-IR spectrometer. The fresh solid catalyst was measured using KBr pellets containing 2.5 mass% samples and prepared by manual grinding using a mortar and pestle. The spectra of solution were recorded as follows: heteropolyacid (0.015 mmol) and cetylpyridinium bromide (0.045 mmol) were dissolved in $H_2O_2$ (0.75 mmol). Then a small amount of solution was spreaded on the surface of a standard KBr flake and immediately subjected to FT-IR measurement.

### 2.6. $^{31}P$ NMR spectra

A 10 ml two-necked round-bottomed flask was charged with heteropolyacid (0.015 mmol), cetylpyridinium bromide (0.045 mmol), *N*,*N*-dimethylformamide (3.0 ml), and $H_2O_2$ (0.75 mmol). The reaction system was maintained at 60 °C and stirred vigorously for 3 h. Then the solution sample was taken and immediately analyzed by $^{31}P$ NMR.

$^{31}P$ NMR spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer, $^{31}P$ chemical shifts are referenced to 85% $H_3PO_4$ as an external standard, and the times of scan was 380.

## 3. Results and discussion

### 3.1. Catalyst characterization

IR (Table 1), UV–vis (Table 4), $^{31}P$ NMR, and elemental analysis data of the 13 HPAs were compared with those of authentic samples and related literature data, clearly indicating that they do have the Keggin structure. Comparison of the IR spectra of the two peroxo complexes with the literature data showed that they were the target compounds.

### 3.2. Optimization of reaction condition

The results of epoxidation of cyclopentene catalyzed by $H_3PMo_{12-n}W_nO_{40}$ combined with CPB with different solvents, temperature, and oxidants are summarized in Tables 2 and 3. The epoxidation catalyzed by the PMW/CPB system, which was carried out in acetonitrile at 60 °C with $H_2O_2$ or urea–hydrogen peroxide adduct (UHP) as oxidant was the optimum. The PMW/CPB system is more active than the $PW_{12}$/CPB system in the epoxidation of cyclopentene. To clarify the mechanism of these reactions, the fresh catalysts and the catalysts under reaction condition were characterized by UV–vis, FT-IR and $^{31}P$ NMR spectroscopies.

### 3.3. UV–vis absorption spectroscopy

A UV–vis study was performed, since most of the heteropolyacids have characteristic spectra in the middle of the ultraviolet range. Table 4 shows the UV spectra data of some $H_3PMo_{12-n}W_nO_{40}$ heteropolyacids combined with CPB measured under the conditions without and with $H_2O_2$ in acetonitrile. Fig. 1 depicts the UV–vis spectra of $PW_{12}$/CPB (a) and $PW_{12}$/CPB treated with an excess of $H_2O_2$ ($[H_2O_2]/[H_3PW_{12}O_{40}] = 50$ mol/mol (b) in acetonitrile. For Fig. 1a of the fresh catalyst, the absorption bands appeared at 265 and 216 nm, respectively. When 50 equiv of $H_2O_2$ was added, the peak at 216 nm shifted to 210 nm. Though the peak at 265 nm still remained, its peak intensity decreased. Comparison between the curves a and b reveals that the structure of $H_3PW_{12}O_{40}$ has changed and the degradation happened by the addition of 50 equiv of $H_2O_2$.

Fig. 2 depicts the UV–vis spectra of PMW/CPB (a) and PMW/CPB treated with 50 equiv of $H_2O_2$ (b) in acetonitrile.

Table 1
FT-IR data of $H_3PMo_{12-n}W_nO_{40}$

| $H_3PMo_{12-n}W_nO_{40}$ | P—O ($cm^{-1}$) | M=O ($cm^{-1}$) | M—$O_b$—M ($cm^{-1}$) | M—$O_c$—M ($cm^{-1}$) |
|---|---|---|---|---|
| $H_3PMo_{12}O_{40}$ | 1063 | 960 | 868 | 783 |
| $H_3PMo_{11}W_1O_{40}$ | 1066 | 964 | 870 | 785 |
| $H_3PMo_{10}W_2O_{40}$ | 1066 | 966 | 869 | 787 |
| $H_3PMo_9W_3O_{40}$ | 1068 | 969 | 872 | 787 |
| $H_3PMo_8W_4O_{40}$ | 1069 | 970 | 873 | 788 |
| $H_3PMo_7W_5O_{40}$ | 1071 | 971 | 876 | 789 |
| $H_3PMo_6W_6O_{40}$ | 1072 | 972 | 877 | 790 |
| $H_3PMo_5W_7O_{40}$ | 1073 | 974 | 878 | 793 |
| $H_3PMo_4W_8O_{40}$ | 1076 | 978 | 880 | 795 |
| $H_3PMo_3W_9O_{40}$ | 1076 | 979 | 882 | 797 |
| $H_3PMo_2W_{10}O_{40}$ | 1077 | 982 | 883 | 800 |
| $H_3PMo_1W_{11}O_{40}$ | 1079 | 983 | 886 | 807 |
| $H_3PW_{12}O_{40}$ | 1080 | 984 | 890 | 809 |

Table 2
Epoxidation of cyclopentene catalyzed by PMW/CPB under different reaction conditions

| Entry | Solvent | Oxidant | Temperature (°C) | Conversion (mol%)[a] | Selectivity (mol%)[b] | Yield (mol%)[c] |
|---|---|---|---|---|---|---|
| 1 | Acetone | $H_2O_2$ | 60 | 13.4 | 43.0 | 5.8 |
| 2 | Methanol | $H_2O_2$ | 60 | 15.8 | 50.9 | 8.0 |
| 3 | Ethyl acetate | $H_2O_2$ | 60 | 19.6 | 52.8 | 10.3 |
| 4 | Benzene | $H_2O_2$ | 60 | 51.5 | 30.0 | 15.4 |
| 5 | 1,2-Dichloroethane | $H_2O_2$ | 60 | 31.3 | 57.0 | 17.8 |
| 6 | Chloroform | $H_2O_2$ | 60 | 44.3 | 82.3 | 36.4 |
| 7 | Acetonitrile | $H_2O_2$ | 60 | 60.2 | 95.5 | 57.5 |
| 8 | Acetonitrile | $H_2O_2$ | 50 | 49.9 | 88.4 | 44.1 |
| 9 | Acetonitrile | $H_2O_2$ | 40 | 41.7 | 90.8 | 37.9 |
| 10 | Acetonitrile | $H_2O_2$ | 30 | 28.3 | 93.8 | 26.5 |
| 11 | Acetonitrile | UHP[d] | 60 | 61.4 | 95.3 | 58.5 |
| 12 | Acetonitrile | *t*-BuHP[e] | 60 | 5.5 | 0 | 0 |
| 13 | Acetonitrile | NaClO | 60 | 6.6 | 0 | 0 |

Reaction conditions: 3 mmol cyclopentene; 0.75 mmol oxidant; 0.015 mmol of $H_3PMo_6W_6O_{40}$ (0.5 mol%); 0.045 mmol cetylpyridinium bromide; 3 ml solvent; 0.52 mmol of *n*-butyl ether as an internal standard; reaction time: 3.5 h.

[a] Conversion/theoretically possible conversion.

[b] Selectivity for cyclopentene epoxide determined by GC analysis.

[c] Conversion × selectivity.

[d] UHP, urea–hydrogen peroxide adduct.

[e] *t*-BuHP, *tert*-butyl hydroperoxide (65%).

Table 3
Epoxidation of cyclopentene catalyzed by heteropolyacids combined with CPB

| Entry | Catalyst | Conversion (mol%) | Selectivity (mol%) | Yields (mol%) |
|---|---|---|---|---|
| 1 | $H_3PMo_{12}O_{40}$ | 3.7 | Trace | Trace |
| 2 | $H_3PMo_{11}W_1O_{40}$ | 24.1 | 83.2 | 20.0 |
| 3 | $H_3PMo_{10}W_2O_{40}$ | 59.8 | 59.5 | 35.6 |
| 4 | $H_3PMo_9W_3O_{40}$ | 49.5 | 62.3 | 30.8 |
| 5 | $H_3PMo_8W_4O_{40}$ | 38.4 | 90.6 | 34.8 |
| 6 | $H_3PMo_7W_5O_{40}$ | 63.2 | 76.0 | 48.0 |
| 7 | $H_3PMo_6W_6O_{40}$ | 60.2 | 95.5 | 57.5 |
| 8 | $H_3PMo_5W_7O_{40}$ | 66.6 | 79.8 | 53.1 |
| 9 | $H_3PMo_4W_8O_{40}$ | 48.8 | 88.3 | 43.1 |
| 10 | $H_3PMo_3W_9O_{40}$ | 51.2 | 71.9 | 36.8 |
| 11 | $H_3PMo_2W_{10}O_{40}$ | 57.9 | 71.9 | 41.6 |
| 12 | $H_3PMo_1W_{11}O_{40}$ | 38.0 | 62.9 | 23.9 |
| 13 | $H_3PW_{12}O_{40}$ | 27.0 | 43.6 | 11.8 |

Reaction conditions: 3 mmol cyclopentene; 0.75 mmol hydrogen peroxide; 0.015 mmol of catalyst (0.5 mol%); 0.045 mmol cetylpyridinium bromide; 3 ml acetonitrile; 0.52 mmol of *n*-butyl ether as an internal standard; reaction temperature: 60 °C; reaction time: 3.5 h.

When no $H_2O_2$ was added, two absorption bands appeared at 225 and 259 nm; the peak intensity of the latter is low. When $H_2O_2$ was added, the peak intensity of the 259 nm band increased and shifted to 265 nm. Though the peak at 225 nm changed little in intensity, but it shifted to 214 nm. These changes indicate the Keggin structure of $H_3PMo_6W_6O_{40}$ has been lost by the action of $H_2O_2$ and to be converted to some new species, which is likely to be the mixture of peroxo anions and undegraded $PMo_6W_6O_{40}{}^{3-}$.

Other $H_3PMo_{12-n}W_nO_{40}$ ($n$ = 1–11) heteropolyacids showed similar changes in UV absorption bands to $H_3PMo_6W_6O_{40}$ when 50 equiv of $H_2O_2$ was added, revealing that these $H_3PMo_{12-n}W_nO_{40}$ are also degraded under the action of hydrogen peroxide.

Table 4
UV absorption spectral data of heteropolyacids in acetonitrile

| Entry | Compound | Absorption (no $H_2O_2$), $\lambda_{max}$ (nm) | Absorption (with $H_2O_2$), $\lambda_{max}$ (nm) |
|---|---|---|---|
| 1 | $H_3PW_{12}O_{40}$ | 216, 265 | 210, 265 |
| 2 | $H_3PMo_1W_{11}O_{40}$ | 212, 260 | 210, 266 |
| 3 | $H_3PMo_3W_9O_{40}$ | 211, 269 | 212, 265 |
| 4 | $H_3PMo_6W_6O_{40}$ | 225, 259 | 214, 265 |
| 5 | $H_3PMo_{11}W_1O_{40}$ | 225, 304 | 215, 266 |
| 6 | $H_3PMo_{12}O_{40}$ | 212, 309 | 211, 310 |

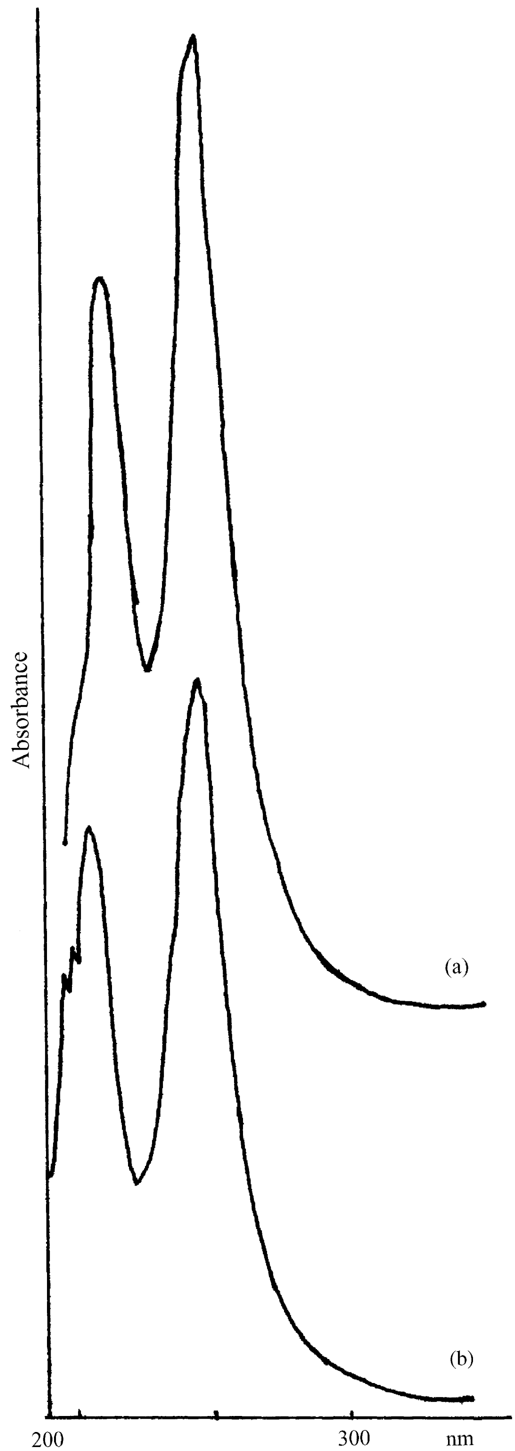


Fig. 1. UV–vis spectra of $H_3PW_{12}O_{40}$ combined with cetylpyridinium bromide in $CH_3CN$: (a) without $H_2O_2$; (b) with 50 equiv of $H_2O_2$.

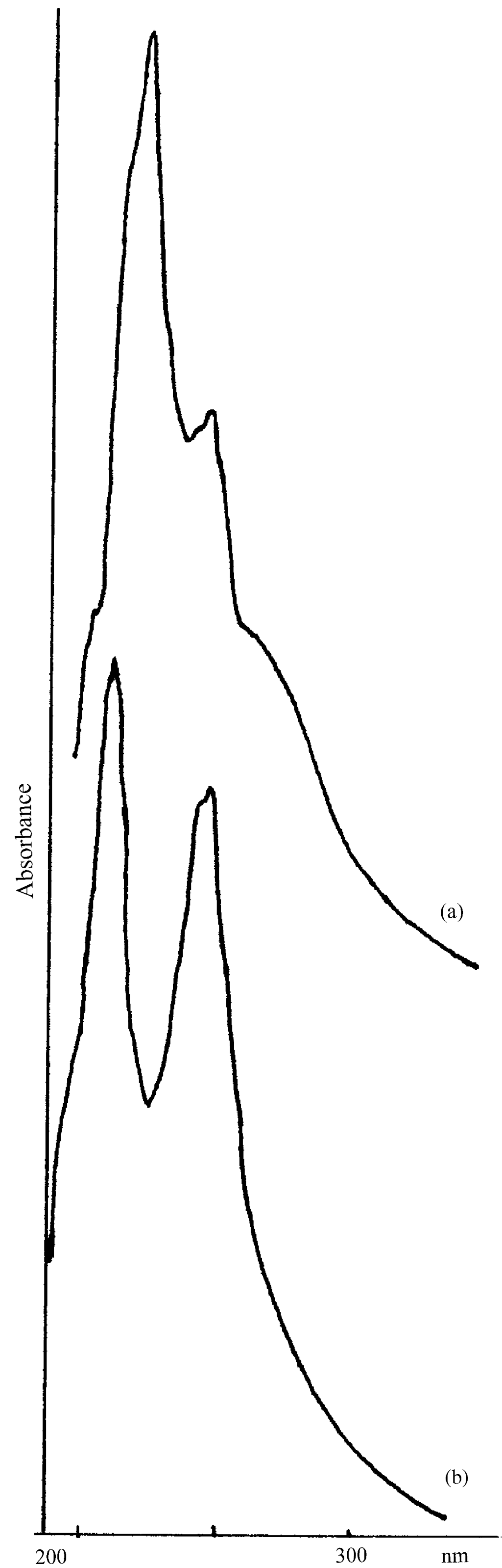


Fig. 2. UV–vis spectra of $H_3PMo_6W_6O_{40}$ combined with cetylpyridinium bromide in $CH_3CN$: (a) without $H_2O_2$; (b) with 50 equiv of $H_2O_2$.

### *3.4. FT-IR spectroscopy*

The FT-IR spectrum of $H_3PMo_6W_6O_{40}$ (Fig. 3a) exhibits four bands at 790, 877, 972, and 1072 $cm^{-1}$ in the fingerprint region. The strong and broad bands at 1072 and 972 $cm^{-1}$ can be ascribed to the stretching mode of the P–O and M=O (Mo or W) bands, respectively.

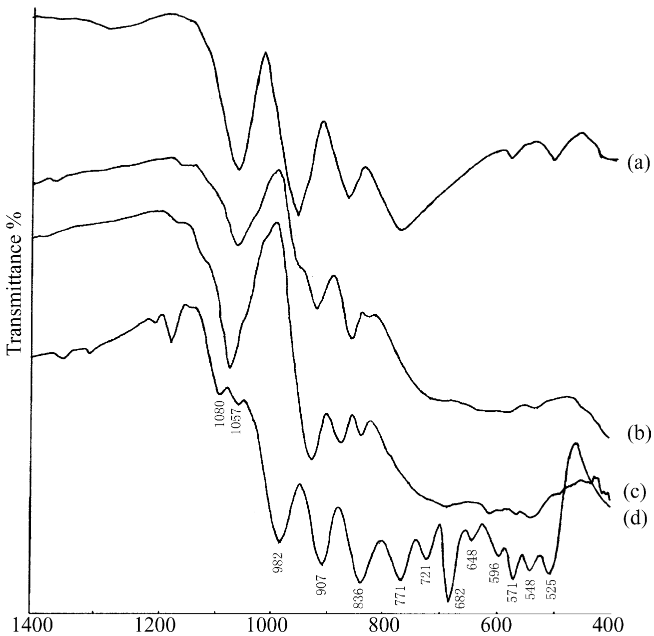


Fig. 3. FT-IR spectra of the catalysts: (a) fresh solid of $H_3PMo_6W_6O_{40}$; (b) $H_3PMo_6W_6O_{40}$ with 50 equiv of $H_2O_2$; (c) $H_3PW_{12}O_{40}$ with 50 equiv of $H_2O_2$; (d) fresh solid of $(CTP)_3\{PO_4[WO(O_2)_2]_4\}$.

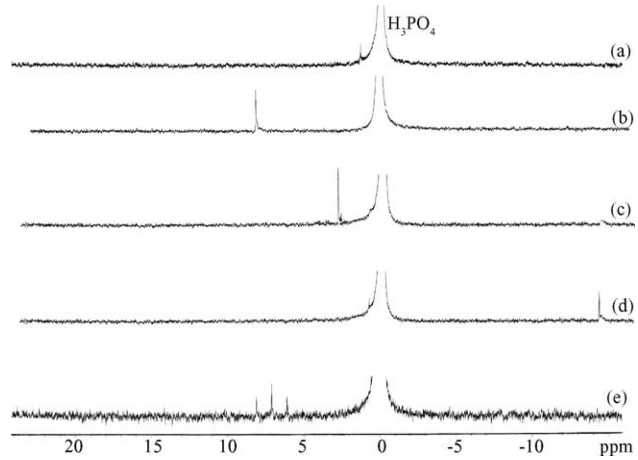


Fig. 4. $^{31}P$ NMR spectra of a DMF solution of various catalysts: (a) PMW + CPB; (b) $(Bu_4N)_3\{PO_4[MoO(O_2)_2]_4\}$; (c) $(CTP)_3\{PO_4[WO(O_2)_2]_4\}$; (d) $PW_{12}$ + CPB + $H_2O_2$; (e) PMW + CPB + $H_2O_2$; spectra are referenced to 85% $H_3PO_4$ as an external standard, 380 scans. The sum of the NMR data acquisition time and the incubation period for each sample was constant in all cases.

The bands at 877 and 790 cm$^{-1}$ can be attributed to the $\nu$ (M–$O_b$–M) (corner-sharing), and $\nu$ (M–$O_c$–M) (edge-sharing) bands, respectively. After the addition of 50 equiv of $H_2O_2$ ($[H_2O_2]/[H_3PMo_{12-n}W_nO_{40}]$ = 50 mol/mol) to the $H_3PMo_6W_6O_{40}$, obvious changes in the origin FT-IR spectrum were observed (Fig. 3b). All the four characteristic bands disappeared and five new bands appeared at 829, 859, 921, 956, and 1063 cm$^{-1}$. The results show that the Keggin structure of $H_3PMo_6W_6O_{40}$ was lost under the action of an excess of $H_2O_2$ and new molybdotungstophosphate species were formed. Comparison of the spectrum with that of $(CTP)_3\{PO_4[WO(O_2)_2]_4\}$ in Fig. 3d indicates that the species degraded from $H_3PMo_6W_6O_{40}$ is obviously not the peroxide.

The FT-IR spectrum of $H_3PW_{12}O_{40}$ shows four bands at 809, 890, 984, and 1080 cm$^{-1}$ in the fingerprint region. The strong and broad bands at 1080 and 984 cm$^{-1}$ can be ascribed to the stretching mode of the P–O and the W=O bands, respectively. The bands at 890 and 809 cm$^{-1}$ can be attributed to the $\nu$ (W–$O_b$–W) (corner-sharing), and $\nu$ (W–$O_c$–W) (edge-sharing) bands, respectively. After the addition of 50 equiv of $H_2O_2$ to $H_3PW_{12}O_{40}$, similar changes happened (Fig. 3c). All the four characteristic bands disappeared and four new bands appeared at 832, 868, 920, and 1062 cm$^{-1}$, suggesting that the Keggin structure of $H_3PW_{12}O_{40}$ has degraded to form new tungstophosphate species, which is different from $(CTP)_3\{PO_4[WO(O_2)_2]_4\}$ as shown by comparison with the spectrum of $(CTP)_3\{PO_4[WO(O_2)_2]_4\}$ (Fig. 3d).

The IR spectra of other $H_3PMo_{12-n}W_nO_{40}$ heteropolyacids changed when 50 equiv of $H_2O_2$ was added, revealing $H_3PMo_{12-n}W_nO_{40}$ heteropolyacids were degraded to form new molybdotungstophosphate species under the action of hydrogen peroxide.

### 3.5. $^{31}P$ NMR spectroscopy

The crystal of $H_3PMo_6W_6O_{40}$ has the α-Keggin structure based on a central $PO_4$ tetrahedron surrounded by $12MO_6$ octahedral arranged in four groups of three edge-shared octahedral $M_3O_{13}$. The groups of $M_3O_{13}$ are linked by sharing corners to each other and to the central $PO_4$ tetrahedron. Mo and W are crystallographically disordered, each M = 1/2Mo + 1/2W, statistically occupying in the crystal [24].

$^{31}P$ NMR spectrum of $H_3PMo_6W_6O_{40}$ exhibits a single line at 1.3 ppm (Fig. 4a). When the catalyst of $H_3PMo_6W_6O_{40}$ combined with cetylpyridinium bromide was treated with 50 equiv of $H_2O_2$ in the absence of substrate, three peaks at 8.1, 7.1, 6.1 ppm (see Fig. 4e) appeared and the peak at 1.3 ppm disappeared. The results show that $H_3PMo_6W_6O_{40}$ has degraded to three phosphorus-containing species. The line at 8.1 ppm can be attributed to $\{PO_4[MoO(O_2)_2]_4\}^{3-}$, the other two lines cannot be assigned at present. The $^{31}P$ NMR chemical shift of $(Bu_4N)_3\{PO_4[MoO(O_2)_2]_4\}$ is located at 8.1 ppm (Fig. 4b). $^{31}P$ NMR spectrum of $H_3PW_{12}O_{40}$ shows a single line at −14.2 ppm. After 50 equiv of $H_2O_2$ was added, a new peak at 0.92 ppm appeared (Fig. 4d). The peak intensity of $[PW_{12}O_{40}]^{3-}$ (−14.2 ppm) is much stronger than that of the new peak, implying that most of $[PW_{12}O_{40}]^{3-}$ is kept and only a small part has degraded. Comparison with the $^{31}P$ NMR spectrum of $(CTP)_3\{PO_4[WO(O_2)_2]_4\}$(2.5 ppm) (Fig. 4c) revealed that the new peak at 0.92 ppm is not the active species of $\{PO_4[WO(O_2)_2]_4\}^{3-}$.

In the above experiments, the sequence of adding reactants was that $H_2O_2$ was added to the mixture of $H_3PW_{12}O_{40}$ and CPB. Now the sequence was changed as follows:

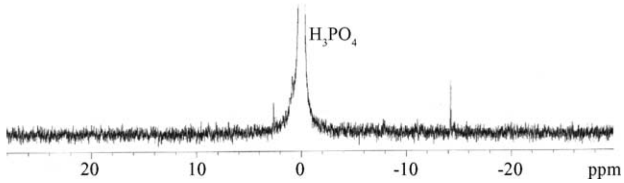


Fig. 5. $^{31}$P NMR spectra of $H_3PW_{12}O_{40}$ treated with 50 equiv of $H_2O_2$, followed by addition of CPB. Spectra are referenced to 85% $H_3PO_4$ as an external standard, 380 scans. The sum of the NMR data acquisition time and the incubation period for each sample was constant in all cases.

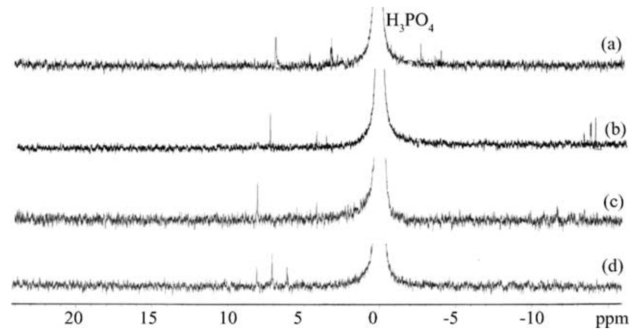


Fig. 6. $^{31}$P NMR spectra of a DMF solution of various catalysts treated with 50 equiv of $H_2O_2$: (a) $H_3PMo_{11}W_1O_{40}$ + CPB + $H_2O_2$; (b) $H_3PMo_1W_{11}O_{40}$ + CPB + $H_2O_2$; (c) $H_3PMo_4W_8O_{40}$ + CPB + $H_2O_2$; (d) PMW + CPB + $H_2O_2$. Spectra are referenced to 85% $H_3PO_4$ as an external standard, 380 scans. The sum of the NMR data acquisition time and the incubation period for each sample was constant in all cases.

first $H_3PW_{12}O_{40}$ (0.015 mmol) was treated with $H_2O_2$ (0.75 mmol), followed by the addition of CPB (0.045 mmol). After 5 min of stirring, DMF (3.0 ml) was added to the mixture, which was stirred for 30 min. Then the solution sample was taken and measured by $^{31}$P NMR. $^{31}$P NMR spectroscopy of thus treated sample exhibits three peaks at −14.2, 0.92, and 2.5 ppm (see Fig. 5). The signal of $\{PO_4[WO(O_2)_2]_4\}^{3-}$ (2.5 ppm) appears, but the peak intensity of $[PW_{12}O_{40}]^{3-}$ (−14.2 ppm) is still stronger than that of the new peaks. This experiment showed that different experimental procedures lead to different phosphorus-containing species.

Under the action of 50 equiv of $H_2O_2$, $[PMo_6W_6O_{40}]^{3-}$ can be degraded completely to form three new phosphorus-containing species, which may be the catalytic-active species in this reaction system. When $H_2O_2$ was added to the mixture of $H_3PW_{12}O_{40}$ and CPB, $[PW_{12}O_{40}]^{3-}$ did not degrade to form the active species of $\{PO_4[WO(O_2)_2]_4\}^{3-}$. These findings may explain the poor activity of $[PW_{12}O_{40}]^{3-}$ in the epoxidation of cyclopentene compared with $[PMo_6W_6O_{40}]^{3-}$.

The $^{31}$P NMR spectra of other $H_3PMo_{12-n}W_nO_{40}$ heteropolyacids are shown in Fig. 6. When $H_3PMo_{11}W_1O_{40}$, $H_3PMo_1W_{11}O_{40}$, and $H_3PMo_4W_8O_{40}$ were treated with 50 equiv of $H_2O_2$, all of them were degraded to several phosphorus-containing species (Fig. 6a–c). A common character is that the species with the Keggin structure were still kept, accompanied with the appearance of new phosphorus-containing species. The $^{31}$P NMR spectrum of the treated sample of $H_3PMo_{11}W_1O_{40}$ exhibits three new peaks at 7.1, 4.6, and 2.8 ppm (Fig. 6a), $H_3PMo_1W_{11}O_{40}$ exhibits three new peaks at 7.4, 4.2, and 3.6 ppm (Fig. 6b), and $H_3PMo_4W_8O_{40}$ exhibits three new peaks at 8.1, 5.5, and 4.2 ppm (Fig. 6c). In the epoxidation system of $H_3PMo_{12-n}W_nO_{40}$ ($n$ = 1–11) combined with CPB, PMW/CPB shows the highest activity. The reasons why PMW/CPB has the highest activity may be explained as follows: when PMW/CPB was treated with 50 equiv of $H_2O_2$, three new phosphorus-containing species produced (the chemical shifts are 8.1, 7.1, and 6.1 ppm). Because the activity of PMW/CPB ranks first, these phosphorus-containing species should be the true active species in the epoxidation. Among the new phosphorus-containing species degraded from $H_3PMo_{11}W_1O_{40}$ (the chemical shifts are 7.1, 4.6, and 2.8 ppm), $H_3PMo_1W_{11}O_{40}$ (the chemical shifts are 7.4, 4.2, and 3.6 ppm) and $H_3PMo_4W_8O_{40}$ (the chemical shifts are 8.1, 5.5, and 4.2 ppm), only one is identical with the species from $H_3PMo_6W_6O_{40}$. Thus the effective active species degraded from $H_3PMo_{11}W_1O_{40}$, $H_3PMo_1W_{11}O_{40}$, and $H_3PMo_4W_8O_{40}$ are fewer than that of the PMW/CPB system, leading to the reaction activities of these catalysts inferior to the latter.

### 3.6. *Epoxidation of other olefins*

The epoxidation of cyclicolefins was carried out in the PMW/CPB and $PW_{12}$/CPB system. All the reactions

Table 5
Epoxidation of alkenes catalyzed by PMW/CPB and $PW_{12}$/CPB system

| Entry | Catalysis system | Substrate | Time (h) | Conversion (mol%) | Selectivity (mol%) |
|---|---|---|---|---|---|
| 1 | PMW/CPB | Cyclopentene | 3.5 | 60.2 | 95.5 |
| 2 | $PW_{12}$/CPB | Cyclopentene | 3.5 | 27.0 | 43.6 |
| 3 | PMW/CPB | Cyclohexene | 3.5 | 60.8 | 90.4 |
| 4 | $PW_{12}$/CPB | Cyclohexene | 3.5 | 90.2 | 64.2 |
| 5 | PMW/CPB | Cyclooctene | 1 | 99.5 | 99.5 |
| 6 | $PW_{12}$/CPB | Cyclooctene | 3 | 99.5 | 95.3 |
| 7 | PMW/CPB | Norbornylene | 3 | 43.4 | 81.5 |
| 8 | $PW_{12}$/CPB | Norbornylene | 3 | 9.6 | 0 |

Reaction conditions: 3 mmol alkene; 0.75 mmol $H_2O_2$; 0.015 mmol of catalyst (0.5 mol%); 0.045 mmol cetylpyridinium bromide; 3 ml solvent; 0.52 mmol of *n*-butyl ether as an internal standard; reaction temperature: 60 °C.

Table 6
Epoxidation of alkenes with $H_2O_2$ catalyzed by $H_3PMo_6W_6O_{40}$ combined with cetylpyridinium bromide

| Entry | Substrate | Time (h) | Conversion (mol%) | Selectivity (mol%) |
|---|---|---|---|---|
| 1 | Cyclopentene | 3.5 | 60 | 96 |
| 2 | Cyclohexene | 3.5 | 61 | 90 |
| 3 | Cyclooctene | 1 | 99 | 99 |
| 4 | Norbornylene | 3 | 43 | 82 |
| 5 | Indene | 3.5 | 42 | 75 |
| 6 | α-Pinene | 4 | 31 | 68 |
| 7 | 6-Methyl-5-hepten-2-one | 5 | 67 | 95 |
| 8 | 1-Octene | 24 | 12 | 93 |
| 9 | 1-Hexene | 24 | 17 | 87 |

Reaction conditions: 3 mmol alkene; 0.75 mmol $H_2O_2$; 0.015 mmol of $H_3PMo_6W_6O_{40}$ (0.5 mol%); 0.045 mmol cetylpyridinium bromide; 3 ml solvent; 0.52 mmol of *n*-butyl ether as an internal standard; reaction temperature: 60 °C.

catalyzed by PMW/CPB system show higher conversion compared with those catalyzed by the $PW_{12}$/CPB system (Table 5). These results further indicate that the species degraded from the PMW/CPB system, whose chemical shifts are 8.1, 7.1, and 6.1 ppm are the true active species under these reaction conditions. The epoxidation of various alkenes including cyclic, chain linear terminal ones and with an electron-withdrawn group were conducted in the PMW/CPB/$H_2O_2$/$CH_3CN$ catalytic system and the results are listed in Table 6. Though the conversion of the chain linear terminal alkenes were low compared with cyclic ones, the selectivity for the desired epoxides were high (∼90%).

## 4. Conclusions

The epoxidation of cyclopentene with hydrogen peroxide catalyzed by 12-heteropolyacids of molybdenum and tungsten ($H_3PMo_{12-n}W_nO_{40}$, $n = 1$–11), $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ combined with cetylpyridinium bromide as a phase transfer reagent was investigated in acetonitrile. The $H_3PMo_6W_6O_{40}$ combined with the CPB system shows the highest activity compared with all the 13 catalytic system. The fresh catalysts and the catalysts under reaction condition were characterized by UV–vis, FT-IR and $^{31}P$ NMR spectroscopy, and it is found that the catalyst $H_3PMo_6W_6O_{40}$ was degraded to three phosphorus-containing species upon the action of 50 equiv of $H_2O_2$, which may be the catalytically active species in these reaction conditions, while most of $H_3PW_{12}O_{40}$ still keep the Keggin structure. Only part of $H_3PW_{12}O_{40}$ degraded to form a phosphorus-containing species, which is not the $\{PO_4[WO(O_2)_2]_4\}^{3-}$ species known as the active species in the Venturello–Ishii system. Different phosphorus-containing species cause the different activity in epoxidation of cyclopentene.

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