Epoxidation of alkenes by hydrogen peroxide over 12-heteropolyacids of molybdenum and tungsten ($H_3PMo_3W_9O_{40}$) combined with cetylpyridinium bromide

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In the epoxidation of 4-vinylcyclohex-1-ene with H_2O_2 in monophasic acetonitrile solution catalysed by Keggin-type 12-heteropolyacids, *i.e.*, $H_3PMo_{12-n}W_nO_{40}$ (n = 0–12), which are precursors of active peroxo complexes, and phase transfer catalysts Q^+Br^-, the catalyst $H_3PMo_3W_9O_{40}$ showed the highest activity, giving a conversion of 98% and a selectivity of 88%. By this method, a variety of water-insoluble unactivated alkenes, internal or terminal, open chain or cyclic and isolated, were epoxidised under mild conditions and after relatively short reaction times. The state of the $H_3PMo_3W_9O_{40}/CPB/H_2O_2/CH_3CN$ system was studied using UV, IR, and ^{31}P NMR spectroscopies with the $[H_2O_2]$:[HPA] ratio = 50. Several peroxo species were observed by ^{31}P NMR spectroscopy at a lower field than the original heteropolyacids. Their composition varied regularly with that of the starting catalyst. The P-containing peroxo species formed were deduced as $[(PO_4)\{Mo_{4-x}W_xO_{20}\}]^{3-}$ (x = 0-4), which are the true catalytically active species under the reaction conditions.

Keywords: epoxidation, $H_3PMo_3W_9O_{40}$, cetylpyridinium bromide, hydrogen peroxide, ^{31}P NMR

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. The oxidation of alkenes with aqueous hydrogen peroxide[1-5] is very attractive from the viewpoint of industrial technology and synthetic organic chemistry since aqueous hydrogen peroxide is cheap, environmentally clean and easy to handle.

Polyoxometalates, as the effective catalysts for epoxidation of alkenes, have drawn wide attention in the last two decades.[6-30] The most significant developments in this field were made by the research groups of Venturello[1,10-11] and Ishii.[12-13] In 1983, Venturello *et al.* showed that the complex consisting of tungstate and phosphate can catalyse the epoxidation of different alkenes with dilute H_2O_2 solution (15%) as oxidant. In 1988, Ishii *et al.* proposed that the system composed of $H_3PW_{12}O_{40}$ and cetylpyridinium chloride can catalyse the epoxidation of alkenes with commercially available H_2O_2 solution (35%) as oxidant in chloroform. In recent years, the epoxidation mechanism with these catalysts has been investigated by many groups.[14-19] It has been proved that $\{PO_4[WO(O_2)_2]_4\}^{3-}$ is the active species in 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 catalytically active intermediates.

However, the major drawback to Venturello–Ishii epoxidations is the necessity of using toxic and carcinogenic chlorocarbons (chloroform or 1, 2-dichloroethane) as solvents.

When we used $H_3PMo_{12-n}W_nO_{40}$ (n = 0–12) combined with cetylpyridinium bromide (abbreviated CPB) as a phase transfer reagent with 50 equivalents of H_2O_2 solution (30%) to catalyse the epoxidation of 4-vinyl-1-cyclohexene in acetonitrile, we found a new phenomenon. The epoxidation was more efficiently catalysed by $H_3PMo_3W_9O_{40}$ combined with CPB than that by $H_3PW_{12}O_{40}$ combined with CPB (abbreviated as the PW_{12}/CPB system). At first the poor reactivity of the PW_{12}/CPB system compared with the $H_3PMo_3W_9O_{40}$/CPB system was difficult to understand. It seems that more active species might result from $H_3PW_{12}O_{40}$ than from $H_3PMo_3W_9O_{40}$.

In an attempt to interpret these results, we characterised the fresh catalysts and the catalysts under the reaction conditions by UV-vis, FT-IR and ^{31}P NMR spectroscopy. It was found that the Keggin-type $H_3PMo_3W_9O_{40}$ is degraded completely in the presence of 50 equivalents of H_2O_2 to form a considerable amount of peroxo phosphorus-containing species. Under the same reaction conditions $H_3PW_{12}O_{40}$ is hardly degraded at all and no $\{PO_4[WO(O_2)_2]_4\}^{3-}$ is detected by ^{31}P NMR spectroscopy.

Experimental

Preparation of heteropolyacids

All solvents 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 the literature,[25] $H_3PMo_{12}O_{40}\cdot nH_2O$ was prepared according to the literature[26] and $H_3PMo_3W_9O_{40}$ was prepared as follows:[25] $Na_2WO_4\cdot 2H_2O$ (15.0 g), $Na_2MoO_4\cdot 2H_2O$ (3.67 g) and $NaH_2PO_4\cdot 2H_2O$ (2.38 g) were dissolved in 66.7 ml of decationised water. The solution was kept at 80°C for 3 h with agitation and then concentrated to 27 ml by evaporation. 33.3 ml of 24% HCl was then added (the solution was yellow) and after extraction with ether at room temperature, crystals were obtained. Yield: 65%.

Other $H_3PMo_{12-n}W_nO_{40}$ (n = 1–11) heteropolyacids were similarly prepared.

$(CTP)_3\{PO_4[WO(O_2)_2]_4\}$ was prepared by a method based on that described by Ishii[13] and $(Bu_4N)_3\{PO_4[MoO(O_2)_2]_4\}$ by a method based on that described by Aubry.[15]

Characterisation techniques

IR, XRD, UV-vis, element analysis and ^{31}P NMR confirmed the formation of the Keggin structure of the free heteropoly acids. Infrared spectra of the heteropoly acids were recorded on a Bruker IFS 120HR spectrometer (0.5 mm KBr pellets containg 2.5 mass % sample). X-ray powder diffraction spectra were measured on a D/Max 2400 Rigaku X-ray diffractometer with Cu–Kα radiation (λ = 0.1542 nm, scan speed 2° (2θ) min^{-1}). Diffuse reflectance UV-vis spectra of the heteropoly compounds dissolved in acetonitrile medium were measured on a Shimadzu UV-240 spectrometer. ^{31}P NMR spectra were recorded on a Varian Unity-300 MHz NMR spectrometer, using *N,N*-dimethylformamide (DMF) as the solvent; ^{31}P chemical shifts are referenced to 85% H_3PO_4 as an external standard. Chemical elemental analysis of the HPAs was done on an ICP-atomic emission spectrometer (ARL 3520 spectrometer), and C, H, and N composition was measured on a German Elementar Vario EL spectrometer.

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Table 1 FT-IR data of $H_3PMo_{12-n}W_nO_{40}$ (n = 0–12)

$H_3PMo_{12-n}W_nO_{40}$	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

Catalytic reactions

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 reaction solution was periodically sampled by a syringe and analysed by a Perkin Elmer XL gas chromatograph equipped with a 15 m SE-54 capillary column and an FID detector. Assignments of products were made by comparison with authentic samples. Selected samples were also analysed by GC/MS (Agilent-6890/5973N).

Experimental procedures A = "without preformation": the heteropoly acid (0.015 mmol) and cetylpyridinium bromide (0.045 mmol) were put in a flask and then acetonitrile (3 ml) was introduced. After stirring for 2 min, 30% H_2O_2 (0.75 mmol) was added. Lastly the alkene (3 mmol) and *n*-butyl ether (0.52 mmol) as an internal standard were added. The reaction mixture was then stirred under reflux at 60°C for 3 h.

Experimental procedures B = "with preformation": the heteropoly acid (0.015 mmol) and cetylpyridinium bromide (0.045 mmol) were put in a flask and then 30% H_2O_2 (0.75 mmol) and urea (0.75 mmol) were added. After 5 min of stirring (necessary for the precursor "to dissolve" completely), the acetonitrile (3 ml) was introduced. Lastly the alkene (3 mmol) and *n*-butyl ether (0.52 mmol) as an internal standard were added. The reaction mixture was then stirred at 60°C for 3 h.

The function of the cetylpyridinium bromide is as a phase transfer catalyst: When reaction initiates, the inorganic peroxo complex which serves as actual epoxidising reagent is formed by the action of hydrogen peroxide with the heteropolyacid, and it is transferred by cetylpyridinium bromide to the solvent phase where epoxidation takes place.

UV-vis measurement

Samples without H_2O_2 added were treated as follows: the 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: the 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.

Table 2 UV absorption spectroscopic data for heteropolyacids in acetonitrile

Entry	Compounds	Absorption (no H_2O_2) λ_{max}/nm	Absorption (with H_2O_2) λ_{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

H_2O_2/heteropolyacid = 50 (molar ratio).

^{31}P NMR spectra

A 10 ml two-necked round-bottomed flask was charged with the 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 a sample of the solution was taken and immediately analysed by ^{31}P NMR.

^{31}P chemical shifts are referenced to 85% H_3PO_4 as an external standard, and the number of scans as 380.

Results and discussion

Catalyst characterisation

IR (Table 1), UV-vis (Table 2), elemental analysis (Table 3) data, and ^{31}P NMR 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.

Optimisation of reaction conditions

The results of the epoxidation of 4-vinyl-1-cyclohexene catalysed by $H_3PMo_{12-n}W_nO_{40}$ combined with CPB with different solvents, and temperature are summarised in Table 4. The epoxidation catalysed by the $H_3PMo_3W_9O_{40}$/CPB system, which was carried out in acetonitrile at 60°C with H_2O_2 was the optimum.

Ultraviolet-visible absorption spectroscopy

A UV-vis study was performed, since most of the heteropolyacids have characteristic spectra in the middle of the UV range. Table 2 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. Figure 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 265nm and 216 nm, respectively. When 50 equivalents of H_2O_2 was added, the peak at 216 nm shifted to 210 nm. Though the peak at 265nm 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 that degradation has occurred on the addition of 50 equivalents of H_2O_2.

Figure 2 depicts the UV-vis spectra of $H_3PMo_3W_9O_{40}$/CPB (a) and $H_3PMo_3W_9O_{40}$/CPB treated with 50 equivalents of H_2O_2 (b) in acetonitrile. When no H_2O_2 was added, two absorption bands appeared at 211nm and 269nm; the peak intensity of the latter is low. When H_2O_2 was added, the peak intensity of the 269nm band increased and shifted to 265 nm. Although the peak at 211nm changed

Table 3 Element analysis data of $H_3PMo_{12-n}W_nO_{40}$ (calculated values)

Catalyst	P (%)	Mo (%)	W (%)
$H_3PMo_{12}O_{40}\cdot 15H_2O$	1.44 (1.48)	54.99 (54.94)	
$H_3PMo_{11}W_1O_{40}\cdot 18H_2O$	1.39 (1.38)	47.10 (47.17)	8.29 (8.22)
$H_3PMo_{10}W_2O_{40}\cdot 20H_2O$	1.35 (1.31)	40.51 (40.63)	15.63 (15.57)
$H_3PMo_9W_3O_{40}\cdot 17H_2O$	1.29 (1.29)	36.00 (36.05)	23.17 (23.03)
$H_3PMo_8W_4O_{40}\cdot 19H_2O$	1.28 (1.23)	30.36 (30.47)	29.11 (29.20)
$H_3PMo_7W_5O_{40}\cdot 16H_2O$	1.23 (1.21)	26.20 (26.31)	35.92 (36.01)
$H_3PMo_6W_6O_{40}\cdot 14H_2O$	1.18 (1.19)	22.03 (22.10)	42.41 (42.35)
$H_3PMo_5W_7O_{40}\cdot 16H_2O$	1.15 (1.14)	17.63 (17.57)	47.27 (47.13)
$H_3PMo_4W_8O_{40}\cdot 15H_2O$	1.15 (1.11)	13.79 (13.71)	52.46 (52.56)
$H_3PMo_3W_9O_{40}\cdot 17H_2O$	1.05 (1.06)	9.71 (9.85)	56.73 (56.62)
$H_3PMo_2W_{10}O_{40}\cdot 15H_2O$	1.06 (1.04)	6.39 (6.45)	61.95 (61.81)
$H_3PMo_1W_{11}O_{40}\cdot 16H_2O$	1.00 (1.01)	3.15 (3.11)	65.57 (65.65)
$H_3PW_{12}O_{40}.20H_2O$	0.97 (0.96)		68.02 (68.09)

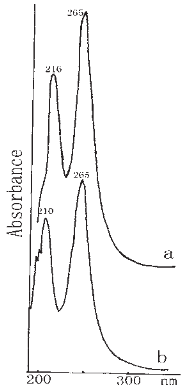


Fig. 1 UV-Vis spectra of $H_3PW_{12}O_{40}$ combined with cetylpyridinium bromide in CH_3CN: (a) without H_2O_2; (b) with 50 equivalents of H_2O_2.

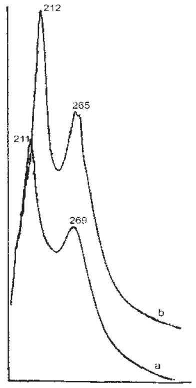


Fig. 2 UV-Vis spectra of $H_3PMo_3W_9O_{40}$ combined with cetylpyridinium bromide in CH_3CN: (a) without H_2O_2; (b) with 50 equivalents of H_2O_2.

Table 4 Epoxidation of 4-vinylcyclohex-1-ene catalysed by $H_3PMo_3W_9O_{40}$/CPB under different reaction conditions[a]

Entry	Solvent	Temperature/°C	Conversion/mol%	Selectivity/mol%
1	Acetone	60	15	38
2	Methanol	60	19	52
3	Ethyl acetate	60	23	49
4	Benzene	60	54	30
5	1,2-dichloroethane	60	37	57
6	Chloroform	60	52	82
7	Acetonitrile	60	98	88
8	Acetonitrile	50	79	89
9	Acetonitrile	40	63	90
10	Acetonitrile	30	45	93

[a]Reaction conditions: 3 mmol 4-vinylcyclohex-1-ene; 0.75 mmol oxidant; 0.015 mmol of $H_3PMo_3W_9O_{40}$ (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 h.

Table 5 Epoxidation of 4-vinylcyclohex-1-ene catalysed by heteropoly acids combined with CTPBr[a]

Entry	Catalyst	Conversion/mol%	Selectivity/mol%[b]	Yields/mol%
1	$H_3PMo_{12}O_{40}$	2	0	0
2	$H_3PMo_{11}W_1O_{40}$	48	52	25
3	$H_3PMo_{10}W_2O_{40}$	55	67	37
4	$H_3PMo_9W_3O_{40}$	58	70	41
5	$H_3PMo_8W_4O_{40}$	31	74	23
6	$H_3PMo_7W_5O_{40}$	73	84	61
7	$H_3PMo_6W_6O_{40}$	69	89	61
8	$H_3PMo_5W_7O_{40}$	31	77	24
9	$H_3PMo_4W_8O_{40}$	34	67	23
10	$H_3PMo_3W_9O_{40}$	98	88	86
11	$H_3PMo_2W_{10}O_{40}$	71	90	64
12	$H_3PMo_1W_{11}O_{40}$	78	88	69
13	$H_3PW_{12}O_{40}$	4	0	0
14	$H_3PW_{12}O_{40}$ + $H_3PMo_{12}O_{40}$(1: 1)	6	0	0

[a]Reaction conditions: 3 mmol 4-vinylcyclohex-1-ene; 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: 3.0 h.

[b]Selectivity to 1,2-epoxy-4-vinylcyclohexane.

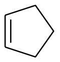
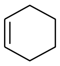
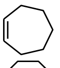
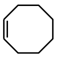
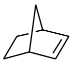
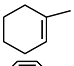
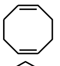
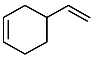
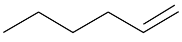
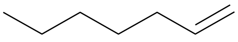
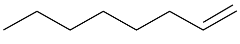
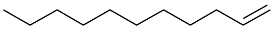
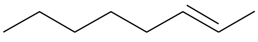
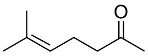
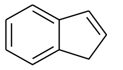
All reactions were carried out according to experimental procedures A.

Table 6 Epoxidation of alkenes catalysed by $H_3PMo_3W_9O_{40}$/CPB and PW_{12}/CPB system[a]

Entry	Catalysis system	Substrate	Conversion/mol%	Selectivity/mol%
1	$H_3PMo_3W_9O_{40}$/CPB	Cyclopentene	83	85
2	PW_{12}/CPB	Cyclopentene	27	43
3	$H_3PMo_3W_9O_{40}$/CPB	Cyclohexene	96	85
4	PW_{12}/CPB	Cyclohexene	90	64
5	$H_3PMo_3W_9O_{40}$/CPB	Cyclooctene	99	99
6	PW_{12}/CPB	Cyclooctene	99	95
7	$H_3PMo_3W_9O_{40}$/CPB	Norbornylene	85	90
8	PW_{12}/CPB	Norbornylene	10	0
9	$H_3PMo_3W_9O_{40}$/CPB	4-vinylcyclohex-1-ene	98	88
10	PW_{12}/CPB	4-vinylcyclohex-1-ene	4	0

[a]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 acetonitrile; 0.52 mmol of *n*-butyl ether as an internal standard; reaction temperature: 60°C; reaction time: 3.0 h.

Table 7 Epoxidation of alkenes with H_2O_2 catalysed by $H_3PMo_3W_9O_{40}$ combined with cetylpyridinium bromide[a]

Entry	Substrate	Experimental procedure[b]	Conversion /mol%	Selectivity /mol%	Yield /mol%
1		A	83	85	71
2		A	96	85	82
3		A	95	91	86
4		A	99	97	96
5		A	85	90	77
6		A	95	93	88
7		A	71	96	68
8		A	98	88	86
9		B	38	91	35
10		B	41	88	36
11		B	45	91	41
12		B	52	86	45
13		B	70	94	66
14		B	62	95	59
15		B	46	87	40

[a]Reaction conditions: 3 mmol alkene; 0.75 mmol H_2O_2; 0.015 mmol of $H_3PMo_3W_9O_{40}$ (0.5 mol%); 0.045 mmol cetylpyridinium bromide; 3 ml solvent acetonitrile; 0.52 mmol of *n*-butyl ether as an internal standard; reaction temperature: 60°C, reaction time: 3 h.
[b]Two experimental procedures: A = without Preformation; B = Preformed catalytic system.

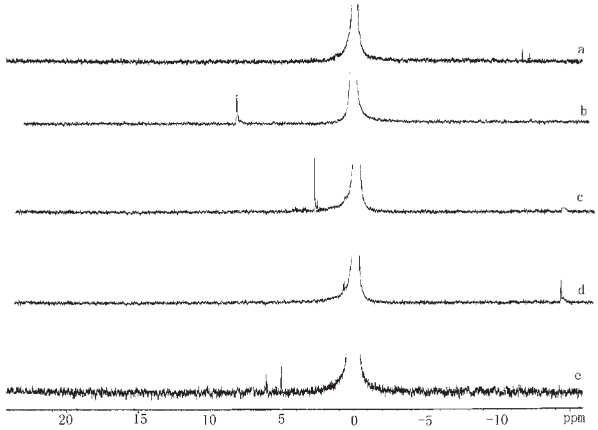


Fig. 3. ^{31}P NMR spectra of a DMF solution of various catalysts: (a) $H_3PMo_3W_9O_{40}$ + CPB; (b) $(Bu_4N)_3\{PO_4[MoO(O_2)_2]_4\}$; (c) $(CTP)_3\{PO_4[WO(O_2)_2]_4\}$; (d) $H_3PW_{12}O_{40}$ + CPB + H_2O_2 (H_2O_2/HPA = 50).; (e) $H_3PMo_3W_9O_{40}$ + CPB + H_2O_2 (H_2O_2/HPA = 50); Spectra are 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.

little in intensity, it shifted to 212 nm. These changes indicate the Keggin structure of $H_3PMo_3W_9O_{40}$ has been lost by the action of H_2O_2 and that it has been converted into some new species which is likely to be a mixture of peroxo anions.

^{31}P NMR spectroscopy

The results of epoxidation of 4-vinylcyclohex-1-ene catalysed by a series of $H_3PMo_{12\text{-}n}W_nO_{40}$ (n = 0–12) combined with CPB in acetonitrile are summarised in Table 5. Among the 13 catalysts, neither $H_3PMo_{12}O_{40}$/CPB (entry 1) nor $H_3PW_{12}O_{40}$/CPB (entry 13) catalysed the epoxidation of 4-vinylcyclohex-1-ene with H_2O_2 under the reaction conditions. The simple mechanical mixture of $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ (1 : 1 in molar ratio) was also inactive for the epoxidation (entry 14). While all molybdotungstophosphoric acids of $H_3PMo_{12\text{-}n}W_nO_{40}$ (n = 1–11) combined with CPB catalysed the epoxidation. Among these heteropoly acids with mixed addenda atoms of Mo and W, $H_3PMo_3W_9O_{40}$, showed the highest activity (entry 10) with a conversion of 98% and a selectivity of 88%.

The epoxidation of cyclic olefins was carried out in the $H_3PMo_3W_9O_{40}$/CPB and PW_{12}/CPB systems. All the reactions catalysed by the $H_3PMo_3W_9O_{40}$/CPB system showed higher yields than those catalysed by the PW_{12}/CPB system (Table 6)

At first sight, the lack of reactivity of the $H_3PW_{12}O_{40}$/CPB system compared with the $H_3PMo_{12\text{-}n}W_nO_{40}$ (n = 1–11)/CPB system is difficult to understand, since $H_3PW_{12}O_{40}$ is catalytically active for the epoxidation reaction under the action of an excess of hydrogen peroxide in a biphasic medium.[13] Evidence[15,19] has shown that heteropolyacids with the Keggin structure, $H_3PW_{12}O_{40}$, are degraded in the presence of an excess of 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 catalytically active intermediates.

In order to interpret these results, we characterised the fresh catalysts and the catalysts under the reaction conditions by ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of $H_3PW_{12}O_{40}$ shows a single line at –14.2 ppm. After 50 equivalents of H_2O_2 were added, a new peak appeared at 0.92 ppm. The peak intensity of $[PW_{12}O_{40}]^{3-}$ (–14.2 ppm) is much higher than that of the new peak, implying that most of $[PW_{12}O_{40}]^{3-}$ remains 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) revealed that the new peak at 0.92 ppm is not the active species of $\{PO_4[WO(O_2)_2]_4\}^{3-}$.

From the ^{31}P NMR analysis it is seen that, under the action of 50 equivalents of H_2O_2, the peaks of $[PMo_3W_9O_{40}]^{3-}$ have disappeared completely and two new peaks at 5.10 and 6.09 ppm have appeared. According to Salles *et al.*,[17,29] the line at 5.10 ppm can be attributed to $[(PO_4)\{Mo_1W_3O_{20}\}]^{3-}$ and that at 6.09 ppm can be attributed to as $[(PO_4)\{Mo_2W_2O_{20}\}]^{3-}$. It seems that just these active species efficiently catalysed the epoxidation of various alkenes in the $H_3PMo_3W_9O_{40}/CPB/H_2O_2/CH_3CN$ system. These findings explain the poor activity of $H_3PW_{12}O_{40}$ in the epoxidation of 4-vinylcyclohex-1-ene compared with $H_3PMo_3W_9O_{40}$.

In order to learn more about the scope of the catalytic activity of the $H_3PMo_3W_9O_{40}/CPB/H_2O_2/CH_3CN$ system and its selectivity, epoxidation was carried out with a variety of alkenes (see Table 7). Cyclic alkenes such as cyclohexene, 1-methylcyclohexene, 4-vinylcyclohex-1-ene, cyclooctene, and norbornene were epoxidised with more than 80% yield. For diene substrates such as 4-vinylcyclohex-1-ene, the C=C moiety with higher electron density was epoxidised regioselectively to give the corresponding monoepoxide. For example, the epoxidation of 4-vinylcyclohex-1-ene mainly affords 1,2-epoxy-4-vinylcyclohexane (86% yield) along with a small amount of the 7,8-oxide and the diepoxide.

Another epoxidation feature of the $H_3PMo_3W_9O_{40}/CPB/H_2O_2/CH_3CN$ system was that nonactivated terminal C_5–C_{11} alkenes such as hex-1-ene, hept-1-ene, oct-1-ene, and undec-1-ene could be transformed to the corresponding epoxide specifically with about 90% selectivity and about 45% conversion after 3 h reaction. For *trans* oct-2-ene, for which the electron density around the C=C bond is higher than that of oct-1-ene, the conversion increased to 70%. Though the conversion of the linear terminal alkenes was not as high as that of the cyclic ones, the selectivity for the desired epoxides was always high (~90%).

Conclusions

The epoxidation of alkenes with hydrogen peroxide catalysed 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 $H_3PMo_3W_9O_{40}$ combined with the CPB system shows the highest activity. The fresh catalysts and the catalysts under reaction condition were characterised by UV-vis, and ^{31}P NMR spectroscopy, and it is found that the catalyst $H_3PMo_3W_9O_{40}$ was degraded to two phosphorus-containing species, $[(PO_4)\{Mo_1W_3O_{20}\}]^{3-}$ and $[(PO_4)\{Mo_2W_2O_{20}\}]^{3-}$ upon the action of 50 equivalents of H_2O_2. These active species efficiently catalysed the epoxidation of various alkenes in the $H_3PMo_3W_9O_{40}/CPB/H_2O_2/CH_3CN$ catalytic system.

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