Lacunary Keggin type polyoxotungstates in conjunction with a phase transfer catalyst: An effective catalyst system for epoxidation of alkenes with aqueous H_2O_2

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A B S T R A C T

$Na_9[SbW_9O_{33}]$ in conjunction with a phase transfer catalyst (methyl tricapryl ammonium chloride) is a highly efficient catalytic system for the selective epoxidation of alkenes with aqueous H_2O_2 as the oxidant. Importantly, the reactions can be carried out in the absence of any organic solvents. The alkene epoxidation reactions with both, a transition metal ion substituted polyoxotungstate as well as a transition metal ion-free polyoxotungstate precursor indicates that the tungstate group is the active center for the oxidation reaction. It was also observed that the transition metal ion does not play any significant role in the reaction. IR studies support the formation of tungsten-peroxo species and also show that the catalyst is stable in the presence of phase transfer catalyst when aqueous H_2O_2 is used as an oxidant.

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1. Introduction

Epoxidation of olefins is one of the most important reactions in organic synthesis as the epoxides are useful intermediates in the manufacturing of a variety of chemicals. Developing new catalysts that will utilize environmental friendly oxidants for alkene epoxidation as an alternative to the stoichiometric oxidation processes still continues to be a subject of interest [1–4]. Many catalysts of metal–organic ligand origin (like metal–salen or metal–porphyrin complexes) are reported for epoxidation of alkenes but the limitations with these catalysts are that the organic part of these catalysts itself is vulnerable to oxidation, thereby reducing its commercial significance. To overcome this problem various approaches have been employed like dispersion of transition metal ions on supports like zeolites, metal oxides, mesoporous materials and so on [5–9]. Alternatively polyoxotungstates based inorganic compounds have been reported in the recent years as efficient catalysts for selective epoxidation reactions [10–14].

Amongst the various polyoxometalates based systems, the transition metal-substituted polyoxometalates (TMSP) like vanadium-substituted phosphomolybdic acid, or the transi-tion metal containing sandwich type polyoxotungstates like $Na_{12}[WZnMn_2(ZnW_9O_{34})_2]$ were found to be robust catalysts for the selective epoxidation of alkenes. Both molecular oxygen and aqueous hydrogen peroxide were used as oxidants. The important advantage of polyoxotungstates is that, they are easy to synthesize as compared to zeolites or other molecular sieves, and are also compatible with aqueous hydrogen peroxide. Hydrogen peroxide is a highly preferred oxidant; owing to the environment friendly nature of its byproduct, i.e. water. Further, with d^0 electronic configuration of tungsten(VI) and molybdenum(VI) species polyoxotungstates do not cause excessive catalytic dismutation of hydrogen peroxide, thus the later is fully available for the epoxidation purpose [12].

Amongst the different types of polyoxometalates, Bosing et al. reported manganese containing sandwich type polyoxometalates with bismuth, antimony or tellurium as the heteroatoms, as efficient catalysts for the regioselective epoxidation of limonene [13]. In liquid–liquid biphasic systems these catalysts in conjunction with a PTC (methyl tricapryl ammonium chloride) displayed very high turn over numbers with aqueous H_2O_2 as the oxidant, and were solvolytically and oxidatively stable. In the present work we have made an attempt to extend their work for the epoxidation of some other alkenes. We have also attempted to study the kinetics of the system as well as to explore the exact role of manganese, and the active intermediates that are responsible for the high activity.

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During the re-investigation of the above catalytic systems, we were astonished to find that the tungsten octahedral clusters are in fact the active centers for the epoxidation of alkenes, irrespective of whichever transition metal or heteroatom that is present. We observed that the extent of limonene epoxidation with both, a manganese ions containing polyoxometalate, i.e. $Na_{11}(NH_4)[Mn_3(H_2O)_3(SbW_9O_{33})_2]$ as well as a manganese ions free polyoxometalate, i.e. $K_{12}[Zn_3(H_2O)_3(SbW_9O_{33})_2]\cdot 48H_2O$ was the same, and so was the activity of the capping agent $Na_9[SbW_9O_{33}]\cdot 19.5H_2O$ itself. This shows that it is the tungstate species that are responsible for the catalytic activity, and not the manganese centers as was thought in the original article. Additionally, in the present studies 1,2-dichloroethane solvent was totally avoided and minimal amount of toluene was used when the alkene was solid (viz. norbornene).

2. Experimental

2.1. Materials

$Na_2WO_4\cdot 2H_2O$, Sb_2O_3, $MnCl_2\cdot 4H_2O$ and $ZnCl_2$ were purchased from Loba Chemie India Ltd. 30% aqueous H_2O_2 was purchased from Merck India Ltd. and the exact strength at the time of usage was determined by common iodometric titration. Substrates used were of highest purity from Aldrich. Aliquat 336 (methyl tricapryl ammonium chloride, hereafter referred as $[MTCA]^+Cl^-$) and chlorobenzene were obtained from S.D. fine chemicals India Ltd.

2.2. Characterization

The IR spectra were recorded on a Shimadzu FTIR 8201 PC instrument. The UV–vis spectra of the catalysts were recorded on a Shimadzu UV-2550 PC UV–vis spectrometer. Thermal analysis was performed on a Seiko model instrument (TG DTA 32) and the thermograms recorded at a heating rate of $10\,K\,min^{-1}$ from 303 to 873 K under N_2 atmosphere. Elemental analysis was performed by alkaline digestion of the polyoxometalate followed by ICP (PerkinElmer Plasma 1000 Emission Spectrometer) for Na, Sb, Mn and Zn, whereas W was determined gravimetrically with 8-hydroxyquinoline. NMR studies were carried out on a Bruker DRX-500 MHz spectrometer.

2.3. Catalyst preparation and catalytic reactions

$Na_9[SbW_9O_{33}]\cdot 19.5H_2O$, $Na_{11}(NH_4)[Mn_3(H_2O)_3(SbW_9O_{33})_2]\cdot 45H_2O$, $K_{12}[Zn_3(H_2O)_3(SbW_9O_{33})_2]\cdot 48H_2O$, $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot 46H_2O$ and $Na_{12}[WZnMn_2(H_2O)_2(ZnW_9O_{34})_2]\cdot 48H_2O$ were prepared as per the literature [12,13,15–17] and their structures were confirmed by IR and elemental analysis. Stock solutions of $[MTCA]_9[SbW_9O_{33}]$ and $[MTCA]_{12}[M_3(SbW_9O_{33})_2]$ (where M = Mn or Zn) were prepared by adopting the reported procedure, where the sodium or potassium ions of $Na_9[SbW_9O_{33}]$ or other polyoxotungstates were quantitatively exchanged with $[MTCA]^+$ ions and extracted into dichloroethane layer [13]. ICP analysis of a well-dried $Na_9[SbW_9O_{33}]$ exchanged 1,2-dichloroethane layer showed the sodium concentration below detection limit, ruling out the possibility of partially exchanged $Na_x[MTCA]_{9-x}[SbW_9O_{33}]$ species.

In a typical catalytic reaction, a 50-ml two-necked round bottom flask equipped with a condenser, was charged with the catalyst stock solution (corresponding to 0.01 mmol of $[MTCA]_9[SbW_9O_{33}]$ or 0.005 mmol of $[MTCA]_{12}[M_3(SbW_9O_{33})_2]$), alkene (5 mmol) and 30% aqueous H_2O_2 (2.5–10 mmol) and 1,2-dichloroethane (5 ml) and then immersed in a previously heated oil bath. For norbornene,

1 ml toluene was used for its dissolution. Alternatively, for epoxidation reaction in the absence of solvent, the round bottom flask was charged with 0.01 mol of $Na_9[SbW_9O_{33}]$ (dissolved in minimum amount of water) and 0.09 mol of $[MTCA]^+Cl^-$, alkene (5 mmol) and 30% aqueous H_2O_2 (2.5–10 mmol). The catalyst will initially be in the aqueous phase but in the presence of PTC, it is pulled into the alkene layer. It may be noted that similar to ICP analysis of 1,2-dichloroethane layers as seen above, even the ICP analysis of alkene layers showed the sodium concentration below detection limit.

The epoxidation reactions were monitored periodically, using GC (Hewlett-Packard 5890 gas chromatograph with a flame ionization detector and $50\,m \times 0.32\,mm$ 5% phenyl methylsilicone capillary column and with N_2 carrier gas), where chlorobenzene was used as the internal reference. Products were unambiguously identified by GC–MS (Shimadzu Gas Chromatograph, GC-17A fitted with QP-500MS Mass Spectrometer) and also with NMR spectroscopy whenever required.

3. Results and discussion

3.1. Role of tungstate species in epoxidation

A manganese ion substituted sandwich type polyoxotungstate, $Na_{11}(NH_4)[Mn_3(H_2O)_3(SbW_9O_{33})_2]$ in conjunction with $[MTCA]^+Cl^-$ (PTC) was reported as a highly efficient catalyst for the epoxidation of limonene with high turnover numbers [13]. Interestingly, the epoxidation was specific to the tri-substituted alkenyl group (forming limonene 1,2-epoxide as the product), as against the di-substituted alkenyl group which gives limonene 8,9-epoxide as the product. The catalyst was found to be stable under the experimental conditions when aqueous H_2O_2 was used as an oxidant. Based on the poor reactivity of the sodium form of the parent precursor, viz. $Na_9[SbW_9O_{33}]\cdot 19.5H_2O$ and the observation of change in the oxidation state of manganese during the reaction from Mn^{2+} to Mn^{3+}, it was postulated that manganese centers play an important role in the epoxidation reaction. We re-investigated this highly efficient and regioselective catalyst to understand the nature of reactive intermediate species responsible for the epoxidation reaction.

Few controlled experiments were carried out to evaluate the catalytic activity of the polyoxotungstate in the absence of manganese ions. Thus, a zinc-based polyoxotungstate $K_{12}[Zn_3(H_2O)_3(SbW_9O_{33})_2]$ (structurally identical to $Na_{11}(NH_4)[Mn_3(H_2O)_3(SbW_9O_{33})_2]$ polyoxotungstate) was synthesized by a reported procedure [15]. Since zinc is not a strong redox centre like manganese, it was chosen as a substitution for this controlled reaction. Thence its activity towards limonene epoxidation was tested in the similar fashion after extraction in dichloroethane with $[MTCA]^+Cl^-$. Surprisingly, the results of zinc-based polyoxometalate were identical to that of the manganese-based polyoxotungstate as can be seen in Table 1. These results indicate that manganese ions may not play any significant role in the above epoxidation reactions, unlike what was mentioned in the original article. In addition, $[MTCA]_9[SbW_9O_{33}]$, formed by mixing aqueous $Na_9[SbW_9O_{33}]\cdot 19.5H_2O$ with $[MTCA]^+Cl^-$ in dichloroethane, which does not contain any other transition metal ion subtituents was also tested as a catalyst for the same epoxidation. However, in order to maintain the same number of tungsten atoms with respect to substrate, twice the number of moles of catalyst was used. Interestingly, the results were identical to that of manganese or zinc-based catalysts ($[MTCA]_{12}[M_3(SbW_9O_{33})_2]$, M = Mn^{2+}, Zn^{2+}) as can be seen in Table 1. Similar experiments were also carried out with $[MTCA]_9[BiW_9O_{33}]$ and $[MTCA]_8[TeW_9O_{33}]$ in dichloroethane and the results obtained were similar to that

Table 1
Controlled experiments for oxidation of limonene using aqueous H_2O_2

Entry	Catalyst	Substrate: catalyst	% conversion	Time (h)
1	$[MTCA]_{12}[(Mn_3(SbW_9O_{33})_2]$ in $C_2H_4Cl_2$	1000:1	90	3
2	$[MTCA]_{12}[(Zn_3(SbW_9O_{33})_2]$ in $C_2H_4Cl_2$	1000:1	91	3
3	$[MTCA]_9[SbW_9O_{33}]$ in $C_2H_4Cl_2$	500:1	92	3
4	$[MTCA]_{12}[WZnMn_2(ZnW_9O_{34})_2]$ in $C_2H_4Cl_2$	1000:1	90	3
5	$Na_9[SbW_9O_{33}] + 9[MTCA]^+Cl^-$ in water	500:1	91	4
6	$Na_9[SbW_9O_{33}] \cdot 19.5H_2O$	100:1	<1	6
7	$MnCl_2 \cdot 4H_2O$	100:1	<1	6
8	$[MTCA]^+Cl^-$	100:1	<1	6

Experimental condition—temp: 60 °C, substrate: 30% aqueous H_2O_2 (mol): 1:2. In all these cases, amounts of catalyst taken were based on the SbW_9O_{33} unit content for a given amount of substrate.

of $[MTCA]_9[SbW_9O_{33}]$ in dichloroethane (not shown here). From the above results we conclude that tungsten octahedrons by themselves are active sites for the epoxidation with aqueous H_2O_2 and there is no additional need of any transition metal ions like Mn^{2+} for the reaction. Similarly, even the antimony, bismuth or tellurium species do not play any major role except that, they help in the formation of the tungstate clusters. Further, these results proved that the 'sandwich' structure is also not essential to demonstrate the catalytic activity for these polyoxotungstates. The change in the oxidation state observed for manganese ions from Mn^{2+} to Mn^{3+} may be an independent reaction in the presence of hydrogen peroxide, which is not surprising.

Thus, the lacunary polyoxotungstate $Na_9[SbW_9O_{33}]$ even in the absence of extra transition metal ion substitutions, in conjunction with $[MTCA]^+Cl^-$ was found to have an excellent catalytic activity upon its extraction in dichloroethane. Hence, after providing sufficient evidence that tungstate species are the active sites, the activity of $Na_9[SbW_9O_{33}]$ in the absence of chlorinated solvents was explored. It was reported that epoxidation of limonene failed in monophasic systems like ethanol or acetonitrile solvent media, while it efficiently worked in liquid–liquid biphasic system with 1,2-dichloroethane solvent [13]. So it is concluded that liquid–liquid biphasic medium was essential for the efficient catalytic activity for this catalytic system. Since limonene and aqueous H_2O_2 form a biphasic mixture, the activity of $Na_9[SbW_9O_{33}]$ in conjunction with $[MTCA]^+Cl^-$ was investigated in the absence of any additional solvent as mentioned in Section 2 and was observed to have worked successfully (see Table 1). It may be noted that similar to limonene, all the alkenes used were typically immiscible with water under reaction conditions and hence the present system is always necessarily a liquid–liquid biphasic system.
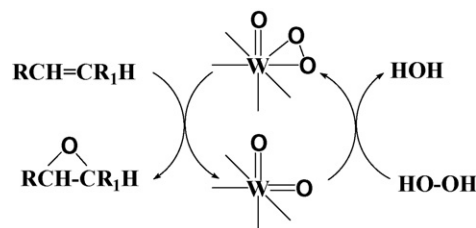
Scheme 1. Proposed model of reaction mechanism for alkene epoxidation (only a single tungsten octahedron is shown for clarity).

However, it was observed that the reaction had slightly slowed down on in situ addition of $Na_9[SbW_9O_{33}]$ and $[MTCA]^+Cl^-$ to limonene as compared to addition of equimolar amount of catalyst stock solution prepared separately by the experimental procedure. This retardation is because of the byproduct NaCl that is formed on mixing $Na_9[SbW_9O_{33}]$ and $[MTCA]^+Cl^-$, as reported earlier [18]. Although the reaction decelerates, no decrease in the final conversion value was observed in the controlled experiments.

3.2. Mechanistic studies

IR spectroscopy was to investigate the nature of active peroxo species, as well as to study the stability of the catalyst under the experimental conditions [12]. Due to the limitation of IR measurement with aqueous solution, IR measurements were made with the dichloroethane solution of $[MTCA]_9[SbW_9O_{33}]$ on KBr discs before and after treating with aqueous H_2O_2 and the spectra can be seen in Fig. 1 (left). The peaks are assigned as follows: 944 (vs) (W–O_t); 880 (vs) (W–O_c–W); 769 (s) (W–O_e–W) (t: terminal, c:
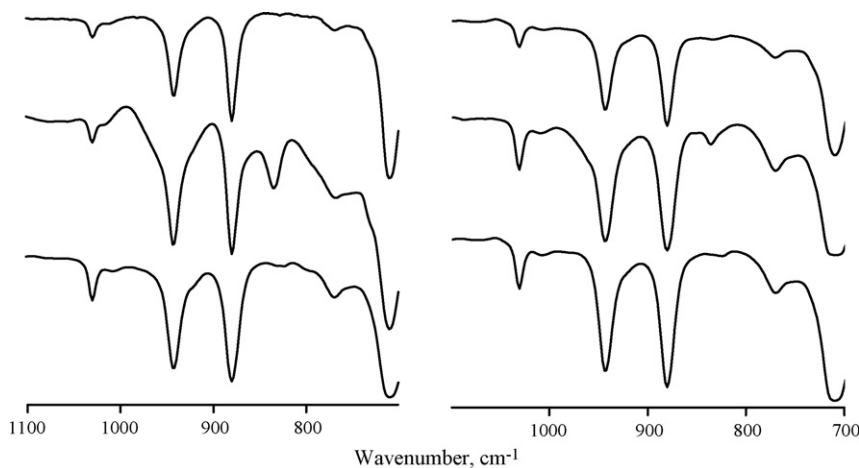

Fig. 1. IR spectra of $[MTCA]_9[SbW_9O_{33}]$ (left) and $[MTCA]_{12}[Mn_3(SbW_9O_{33})_2]$ (right) in 1,2-dichloroethane (top: before reaction, center: after addition of 30% aqueous H_2O_2, bottom: after decomposition of excess of peroxide with 10% KI solution).
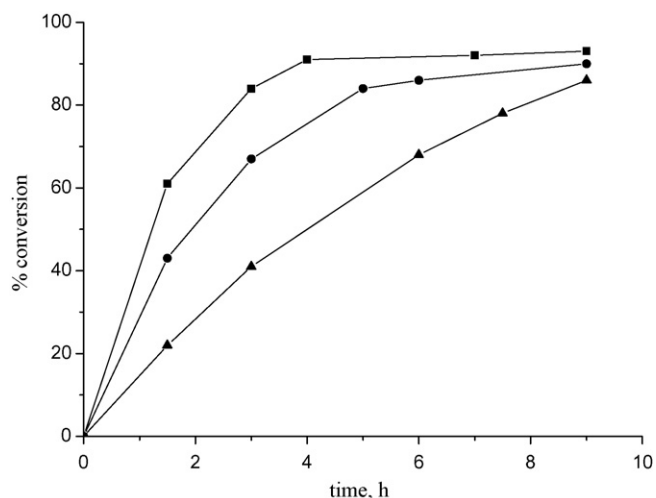
Fig. 2. Kinetic plots of epoxidation of limonene over $Na_9[SbW_9O_{33}] + 9[MTCA]^+Cl^-$ at different temperatures in the range 35–60 °C. *Reaction conditions*—$Na_9[SbW_9O_{33}]$: 0.01 mmol, $[MTCA]^+Cl^-$: 0.09 mmol, limonene: 5 mmol and 30% aqueous H_2O_2: 10 mmol (▲: 35 °C, ●: 50 °C and ■: 60 °C).

corner sharing, e: edge sharing). An additional peak appearing at 834 cm^{-1} after the above solution was treated with aqueous H_2O_2, is attributed to the formation of tungsten-peroxo species in accordance with the literature [12,19]. On treatment with 10% aqueous KI, the peroxide decomposes and the peak at 834 cm^{-1} disappears. The resultant spectrum was identical to that of the fresh sample as can be seen in the figure. Similar spectral measurements were also done with dichloroethane solution of $[MTCA]_{12}[Mn_3(SbW_9O_{33})_2]$ and the spectra were identical to $[MTCA]_9[SbW_9O_{33}]$ spectra (Fig. 1, right). These studies indicate that tungsten-peroxo species was the possible intermediate species involved in the selective oxidation of alkenes, and the results also prove that the catalyst is stable under the present experimental conditions. Further, our efforts to isolate the peroxo intermediate presumably forming during the hydrogen peroxide treatment with $[MTCA]_9[SbW_9O_{33}]$ in dichloroethane solvent became futile. However, number of peroxo species formed was estimated to be six per unit of $[SbW_9O_{33}]$ by titration between

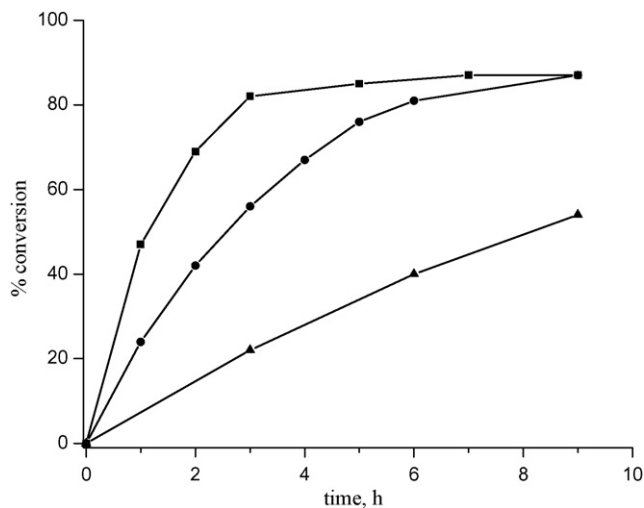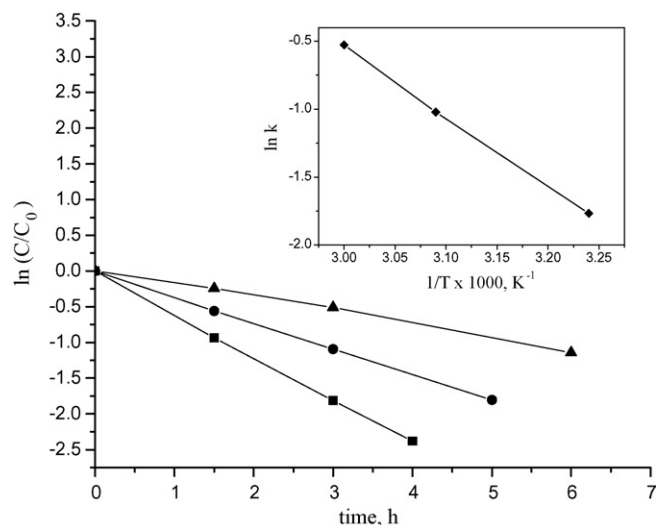**Fig. 4.** Kinetic profiles of limonene epoxidation reaction as a function of temperature and their linear fittings. *Reaction conditions*—catalyst: 0.01 mmol, $[MTCA]^+Cl^-$: 0.09 mmol, limonene: 5 mmol and 30% aqueous H_2O_2: 10 mmol (▲: 35 °C, ●: 50 °C and ■: 60 °C). Inset: a plot of measured rate constants as a function of temperatures in an Arrhenius plot.

dichloroethane solutions of the peroxo intermediate complexes with methanolic Ce(IV) [20].

Finally, on the basis of IR observations we propose a model to the reaction mechanistic pathway for the epoxidation of alkenes as shown in Scheme 1. One or more tungstate octahedron of the $Na_9[SbW_9O_{33}]$ cluster bind to peroxo species with possible seven coordination and the original structure is retained on the completion of oxidation reaction.

3.3. Epoxidation of other alkenes

The conversion values increased with rise in temperature for all the alkenes. Figs. 2 and 3 show the typical trend for limonene
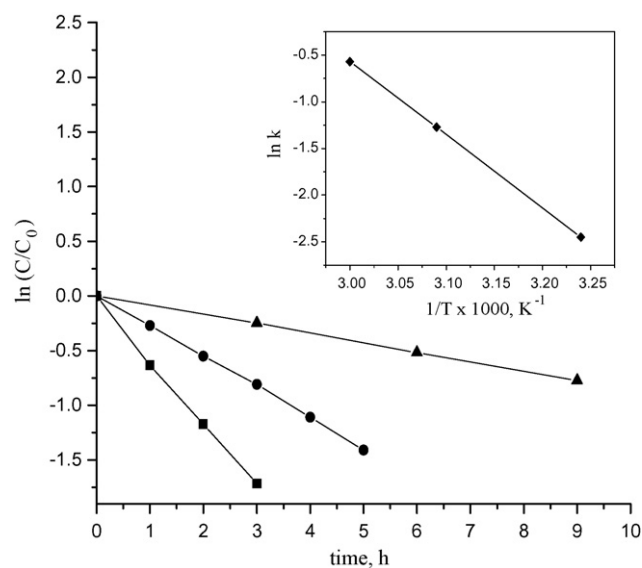

Fig. 3. Kinetic plots of epoxidation of norbornene over $Na_9[SbW_9O_{33}] + 9[MTCA]^+Cl^-$ at different temperatures in the range 35–60 °C. *Reaction conditions*—$Na_9[SbW_9O_{33}]$: 0.01 mmol, $[MTCA]^+Cl^-$: 0.09 mmol, norbornene: 5 mmol, 30% aqueous H_2O_2: 5 mmol and toluene: 1 ml (▲: 35 °C, ●: 50 °C and ■: 60 °C).

Fig. 5. Kinetic profiles of norbornene epoxidation reaction as a function of temperature and their linear fittings. *Reaction conditions*—catalyst: 0.01 mmol, $[MTCA]^+Cl^-$: 0.09 mmol, norbornene: 5 mmol, 30% aqueous H_2O_2: 5 mmol and toluene: 1 ml (▲: 35 °C, ●: 50 °C and ■: 60 °C). Inset: a plot of measured rate constants as a function of temperatures in an Arrhenius plot.
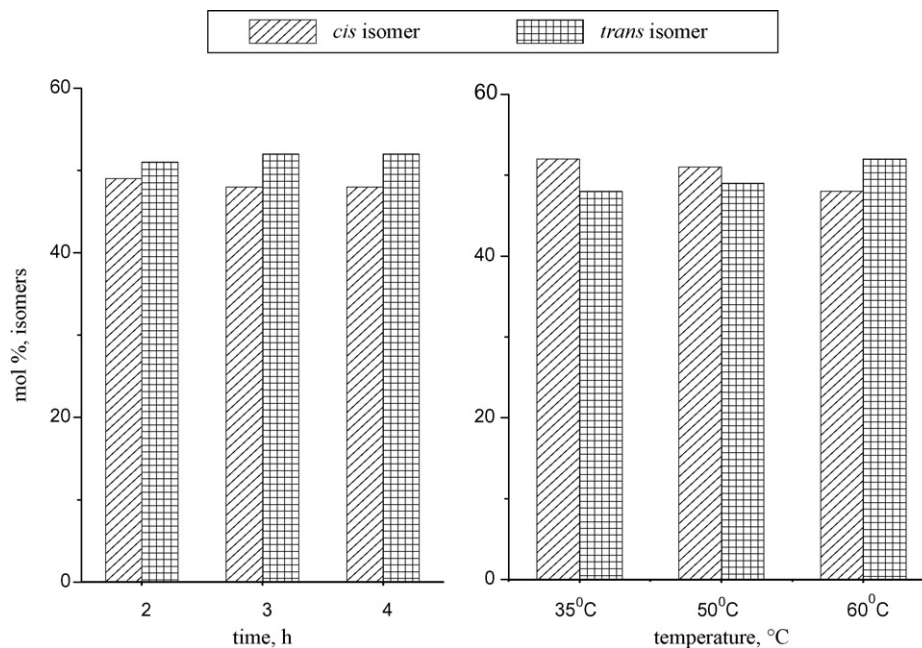
Fig. 6. Selectivity of *cis*- and *trans*-isomers of limonene 1,2-epoxide—(a) left: with time at maximum conversion, *reaction conditions*—Na$_9$[SbW$_9$O$_{33}$]: 0.01 mmol, [MTCA]$^+$Cl$^-$: 0.09 mmol, limonene: 5 mmol, 30% aqueous H$_2$O$_2$: 10 mmol and temp: 60 °C. (b) Right: with reaction temperature at the maximum conversion, *reaction conditions*—Na$_9$[SbW$_9$O$_{33}$]: 0.01 mmol, [MTCA]$^+$Cl$^-$: 0.09 mmol, limonene: 5 mmol and 30% aqueous H$_2$O$_2$: 10 mmol.

Table 2
Oxidation of various alkenes over Na$_9$[SbW$_9$O$_{33}$] + 9[MTCA]$^+$Cl$^-$ with aqueous H$_2$O$_2$ as oxidant at different temperatures and different substrate: oxidant ratios

Substrate	Substrate: aqueous H$_2$O$_2$	Temp (°C)	Time (h)	Conversion (%)	Selectivity (%)
Limonene	1:2	60	4	91	*cis*-Limonene 1,2-epoxide (49) *trans*-limonene 1,2-epoxide (51)
Norbornene[a]	1:1	60	5	85	Norbornene epoxide (80) Norbornanone (20)
Norbornene[a]	1:2	60	5	87	Norbornene epoxide (11) Norbornanone (89)
Cyclohexene	1:1	35	6	42	Cyclohexene epoxide (25) Cyclohexene-2-ol (41) Cyclohexene-2-one (34)
Cyclohexene	1:0.5	35	6	24	Cyclohexene epoxide (92) Cyclohexene diol (8)
Cyclooctene	1:1	60	6	97	Cyclooctene epoxide (>99)
Cyclooctene	1:2	35	9	95	Cyclooctene epoxide (>99)
cis-Stilbene	1:2	60	6	57	*cis*-Stilbene epoxide (88) *trans*-stilbene epoxide (12)
1-Octene	1:2	60	9	38	1-Octene epoxide (>99)

Reaction conditions—Na$_9$[SbW$_9$O$_{33}$]: 0.01 mmol, [MTCA]$^+$Cl$^-$: 0.09 mmol, substrate: catalyst ratio (500:1).

[a] 1 ml toluene was used as solvent.

and norbornene, respectively. Accordingly, the energy of activation was determined graphically for these two substrates and the values were found to be 10.2 and 15.6 kcal K^{-1} mol^{-1}, respectively (Fig. 4 for limonene and Fig. 5 for norbornene). The activation energy although low for catalytic reactions in general is quite typical for biphasic oxidation reactions [12]. Similarly, the values of the enthalpy of activation determined for limonene and norbornene were 9.6 and 15.0 kcal K^{-1} mol^{-1} respectively. In the case of limonene, stereoisomers of limonene-1,2-oxide was the only product obtained. No traces of limonene-8,9-oxide or limonene di-epoxide were observed in the product mixture indicating the catalyst is highly efficient for regioselective epoxidation reactions of such dienes, as reported in the original article [13]. Limonene-1,2-epoxide existed in both *cis*- and *trans*-isomeric forms in almost an equimolar ratio as can be seen in Fig. 6.

In case of norbornene and cyclohexene, a lower substrate: oxidant ratio gave excellent selectivity for the epoxide as can be seen in Table 2. On increasing the substrate: oxidant ratio, cyclohexene chiefly underwent allylic oxidation while norbornene mainly gave norbornanone. Similarly, increase in the temperature also favors allylic oxidation of the former, also reported by others [12]. Another cyclic alkene, viz. cyclooctene gave only the epoxide with near quantitative yields, even at ambient temperature conditions.

Cyclooctene has no tendency of undergoing allylic oxidation or cleaving of the epoxide like cyclohexene [21].

Terminal alkenes are normally very less reactive, but with our catalytic system 1-octene gave a moderate conversion of 38% and showed >99% selectivity for the epoxide. With an activated terminal alkene like styrene, instead of epoxide formation the olefinic bond was cleaved and benzaldehyde was obtained as the major product. Another activated alkene, viz. *cis*-stilbene gave a mixture of both *cis*-stilbene oxide (88% selectivity) and *trans*-stilbene oxide (balance) as products at the maximum conversion of the substrate (ca. 57%). *trans*-Stilbene on the other hand, gave only benzaldehyde as the product with very poor conversion (not shown here).

4. Conclusions

The results clearly indicate that Na$_9$[SbW$_9$O$_{33}$] in conjunction with a phase transfer catalyst [MTCA]$^+$Cl$^-$ is capable of epoxidizing a number of structurally different alkenes in high yields. In most of the cases the selectivity for epoxide was excellent. Importantly, there is no need of any solvent for the reaction (except when the alkene is a solid). It can be unambiguously seen from the controlled experiments that tungstate species are indeed the active center and transition metal ions do not play any major role. The IR studies

indicate the formation of a tungsten-peroxo intermediate on the interaction of polyoxotungstate with aqueous H_2O_2 in presence of [MTCA]$^+$Cl$^-$, and this intermediate was observed for both the transition metal containing polyoxotungstate as well as the transition metal free precursor. IR studies also reveal that the catalyst is stable in the presence of PTC when aqueous H_2O_2 was used as the oxidant.

Acknowledgements

References

[1] R. Neumann, A.M. Khenkin, Inorg. Chem. 34 (1995) 5753.
[2] R.S. Drago, Coord. Chem. Rev. 117 (1992) 185.
[3] B. Meunier, Chem. Rev. 92 (1992) 1411.
[4] Cytochrome P-450, Structure, Mechanism and Biochemistry, P.R. Ortizde Montellano (Ed.), Plenum Press, New York, London, 1986, pp. 1–28.
[5] M.J. Naughton, R.S. Drago, J. Catal. 155 (1995) 383.
[6] J.P. Arhancet, M.E. Davis, J.S. Merola, B.E. Hanson, Nature 339 (1989) 454.
[7] G.A. Ozin, C. Gil, Chem. Rev. 89 (1989) 1749.
[8] E. Byambajav, Y. Ohtsuka, Appl. Catal. A: Gen. 252 (2003) 193.
[9] R. Grommen, P. Manikandan, Y. Gao, T. Shane, J.J. Shane, R.A. Schoonheydt, B.M. Weckhuysen, D. Goldfarb, J. Am. Chem. Soc. 122 (2000) 11488.
[10] D. Mansuy, J.-F. Bartoli, P. Battioni, D.K. Lyon, R.G. Finke, J. Am. Chem. Soc. 113 (1991) 7222.
[11] N.K.K. Raj, A.V. Ramaswamy, P. Manikandan, J. Mol. Catal. A: Chem. 227 (2004) 37.
[12] R. Neumann, M. Gara, J. Am. Chem. Soc. 117 (1995) 5066.
[13] M. Bösing, A. Nöh, I. Loose, B. Krebs, J. Am. Chem. Soc. 120 (1998) 7252.
[14] R. Neumann, M. Dahan, J. Am. Chem. Soc. 120 (1998) 11969.
[15] U. Kortz, N.K. Al-Kassem, M.G. Savelieff, N.A.A. Kadi, M. Sadakane, Inorg. Chem. 40 (2001) 4742.
[16] M. Bosing, L. Loose, H. Pohlmann, B. Krebs, Chem. Eur. J. 3 (1997) 1232.
[17] C.M. Tourné, G.F. Tourné, F. Zonnevijlle, J. Chem. Soc., Dalton Trans. (1991) 143.
[18] K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, R. Noyori, J. Org. Chem. 61 (1996) 8310.
[19] J. Gao, Y. Chen, B. Han, Z. Feng, C. Li, N. Zhou, S. Gao, Z. Xi, J. Mol. Catal. A: Chem. 210 (2004) 197.
[20] A.I. Vogel, A Text-book of Quantitative Inorganic Analysis, Third ed., Longman, London, 1961.
[21] A.J. Appleton, S. Evans, J.R.L. Smith, J. Chem. Soc., Perkin Trans-2 (1996) 281.