Chapter 2:

Selective oxidation of alkenes and alcohols over [SbW$_9$O$_{33}$] based catalyst system with aq. H$_2$O$_2$

2.1 Introduction

Epoxidation of olefins is one of the most studied reactions in organic synthesis, as the epoxides are useful intermediates in the manufacturing of a variety of chemicals. Similarly, selective oxidation of alcohols to their carbonyls is also of paramount importance in organic synthesis. Generally all these oxidation reactions involve stoichiometric quantities of inorganic/organic oxidants [1], toxic or hazardous oxidizing agents [2-5]. Developing new catalysts that will utilize environmental friendly oxidants for these oxidation reactions, as an alternative to the stoichiometric oxidation processes still continues to be a subject of interest [6-9]. Many catalysts of metal-organic ligand origin (like metal-salen or metal-porphyrin complexes) are reported for epoxidation of alkenes and oxidation of alcohols, but the limitations with these catalysts are that the organic part of these catalysts itself is vulnerable to oxidation, thereby reducing its activity significantly. To overcome this problem various approaches have been employed like dispersion of transition metal ions on inert supports like zeolites, metal oxides, mesoporous materials and so on [10-14]. Alternatively polyoxotungstates based inorganic compounds have been reported in the recent years as efficient catalysts for selective oxidation reactions [15-19].

Amongst the various polyoxometalates based systems, the transition metal substituted polyoxometalates (TMSP) like vanadium substituted phosphomolybdic acid, or the transition 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 as well as oxidation of alcohols. 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. While aerobic oxidation is certainly important, there are also certain advantages with H_2O_2 as the oxidants [20]. Hydrogen peroxide is preferred as an oxidant since it is cheap, environmental friendly and contains a high percentage of active oxygen. 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 oxidation purpose [17].

Amongst the different types of polyoxometalates, manganese containing sandwich type polyoxometalates with bismuth, antimony or tellurium as the

heteroatoms reported by Bosing *et al* were found to highly efficient catalysts for the regioselective epoxidation of limonene [18]. In liquid-liquid biphasic systems these catalysts in conjunction with a methyl tricapryl ammonium chloride (PTC) displayed very high turn over numbers with *aq.* H_2O_2 as the oxidant, and were solvolytically and oxidatively stable. In the present chapter we have made an attempt to extend their work for the epoxidation of some other alkenes. We have also attempted the kinetic studies of the system as well as to explore the exact role of manganese, and the active intermediates that are responsible for the high activity.

During the re-investigation of the above catalytic systems, we were surprised to find that the tungsten octahedral clusters are in fact the active centers for the epoxidation of alkenes or oxidation of alcohols, irrespective of whichever transition metal or heteroatom that is present. We observed that the magnitude of limonene epoxidation with a manganese ions containing polyoxometalate *i.e.* $Na_{11}(NH_4)[Mn_3(H_2O)_3(SbW_9O_{33})_2]$ as well as with a manganese ions free polyoxometalate *i.e.* $K_{12}[Zn_3(H_2O)_3(SbW_9O_{33})_2].48H_2O$ was the same, and so was the activity of the capping agent $Na_9[SbW_9O_{33}].19.5H_2O$ itself. This shows that it is the tungstate species that are responsible for the catalytic activity, and not the manganese species as was believed in the original article.

Additionally, in the present studies 1,2-dichloroethane solvent was totally avoided and minimal amount of toluene was used whenever the substrate was a solid. Further, apart from alkenes, an attempt was made to extrapolate the activity of $Na_9[SbW_9O_{33}].19.5H_2O$ towards the oxidation of a variety of secondary and allylic alcohols, which also worked successfully, as shall be seen in the further sections.

2.2 Experimental

2.2.1 Materials

Sodium tungstate dihydrate, Sb_2O_3, $MnCl_2.4H_2O$ and $ZnCl_2$ were purchased from Loba Chemie Ltd, India. *Aq.* H_2O_2 (30 %) was purchased from Merck and exact strength at the time of usage was determined by iodometric titration. Substrates (both alkenes and alcohols) used were of highest purity purchased from Aldrich. Aliquat 336 (methyl tricapryl ammonium chloride) and chlorobenzene were obtained from S. D. fine chemicals India Ltd.

2.2.2 Catalyst synthesis

2.2.2.1 Synthesis of Na₉[SbW₉O₃₃].19.5H₂O

This compound was prepared by reaction of $Na_2WO_4.2H_2O$ (40 g, 121 mmol) in boiling water (80 ml) and drop wise addition of Sb_2O_3 (1.96 g, 6.72 mmol) dissolved in concentrated HCl (12 M, 10 ml). The mixture was refluxed for 1 h and was allowed to cool slowly. Colorless crystals of $Na_9[SbW_9O_{33}].19.5H_2O$ were formed after evaporation of one-third of the solution volume. Yield: 28.0 g (72 %). In a similar manner $Na_9[BiW_9O_{33}]$ and $Na_8[TeW_9O_{33}]$ were synthesized to perform some controlled reactions as shall be seen further.

2.2.2.2 Synthesis of Na₁₁(NH₄){[Mn(H₂O)]₃(SbW₉O₃₃)₂}.45H₂O

$Na_9[SbW_9O_{33}].19.5H_2O$ (4 g, 1.4 mmol) was dissolved in water (8 ml) under gentle heating. To this pale yellow mixture was given slowly a solution of $MnCl_2.4H_2O$ (0.414 g, 2.08 mmol) in water (10 mL), leading to a deep orange solution with pH 6-7. The mixture was refluxed for 1 h, and then NH_4NO_3 (0.673 g, 8.4 mmol) was added. After the mixture was cooled to ambient temperature, dark orange crystals of $Na_{11}(NH_4)\{[Mn(H_2O)]_3(SbW_9O_{33})_2\}.45H_2O$ were obtained after several days. Yield: 2.6 g (63%). In a similar manner, $Na_{12}\{[Cu(H_2O)]_3(SbW_9O_{33})_2\}$ and $Na_{12}\{[Co(H_2O)]_3(SbW_9O_{33})_2\}$ were synthesized to perform some controlled reactions as shall be seen further.

2.2.2.3 Synthesis of K₁₂{[Zn(H₂O)]₃(SbW₉O₃₃)₂}.46H₂O

A sample of $ZnCl_2$ (0.92 g, 6.7 mmol) was dissolved in 50 ml of H_2O and to it was added $Na_9[SbW_9O_{33}].19.5H_2O$ (10.0 g, 4.1 mmol) dissolved in water (20 ml) was added drop wise. The solution was refluxed for 1 h and filtered after cooling (pH 6.6). The potassium salt of the heteropoly anion was isolated in high yield by precipitation of the above solution with solid KCl (15 g). This resulted in a white product, which was isolated and air-dried. Yield: 9.5 g (83%).

2.2.3 Characterization of the catalysts

The catalysts were subjected to elemental analysis and FT-IR for the confirmation of products formed. Elemental analysis of sodium, potassium, manganese, zinc, antimony, tellurium and bismuth was carried out by inductively

coupled plasma spectroscopy (ICP). The ICP was performed on Perkin Elmer Plasma Emission 1000 Spectrometer. Tungsten was estimated by gravimetric analysis using 8-hydroxyquinoline as the precipitating agent. The number of water molecules was determined by TG-DTA and were in agreement with the reported ones. The 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. FT-IR spectra were recorded on a Shimadzu FTIR 8201 PC instrument. The FT-IR spectra were recorded as KBr pellets.

2.2.4 Catalytic reactions

2.2.4.1 Preparation of catalyst stock solutions

[MTCA]₉[SbW₉O₃₃],   [MTCA]₉[BiW₉O₃₃],   [MTCA]₈[TeW₉O₃₃], [MTCA]₁₂[Mn₃(SbW₉O₃₃)₂], [MTCA]₁₂[Cu₃(SbW₉O₃₃)₂], [MTCA]₁₂[Co₃(SbW₉O₃₃)₂] and [MTCA]₁₂[Zn₃(SbW₉O₃₃)₂] were prepared by exchanging the sodium or potassium ions from the appropriate aqueous heteropoly salts with MTCA$^+$, and extracting the same into $C_2H_4Cl_2$ layer. Thus 0.064 mol of the alkali salt of polyoxometalate, dissolved in 10 ml of water was exchanged with 0.512 or 0.576 or 0.768 (depending on the charge on heteropoly anion) of [MTCA]$^+$Cl$^-$ dissolved in 10 ml of dichloroethane. ICP analysis of a well dried Na₉[SbW₉O₃₃] exchanged 1,2 dichloroethane layer showed the sodium concentration beyond detection limit, ruling out the possibility of partially exchanged Na$_x$[MTCA]₉₋ₓ[SbW₉O₃₃] species.

2.2.4.2 Procedure for the epoxidation of alkenes

The alkenes considered here for the epoxidation studies were limonene, norbornene, cyclooctene, cyclohexene, *cis*-stilbene, *trans*-stilbene, styrene and 1-octene. 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[XW₉O₃₃] where X: Sb, Bi, Te or 0.005 mmol of [MTCA]₁₂[M₃(SbW₉O₃₃)₂] where M: Mn, Co, Cu, Zn), alkene (5 mmol), 30% *aq*. H₂O₂ (2.5 to 10.0 mmol) 1,2 dichloroethane (5 ml) and 30% *aq*. H₂O₂ (2.5 to 10.0 mmol), and further heated to the required reaction temperature with constant stirring. Alternatively, for epoxidation reaction in the absence of solvent, the round bottom flask was charged with 0.01 mol of Na₉[SbW₉O₃₃] (dissolved in minimum amount of water) and 0.09 mol of [MTCA]$^+$Cl$^-$, alkene (5.0 mmol) and 30% *aq*. H₂O₂

(2.5 to 10.0 mmol). For norbornene and *trans*-stilbene, 1 ml toluene was used for its dissolution. 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 beyond detection limit.

2.2.4.3 Procedure for the oxidation of alcohols

In a typical catalytic reaction, a 25 ml two-necked round bottom flask equipped with a condenser was charged with 0.01 mole of $Na_9[SbW_9O_{33}]$ and 0.09 mole of $MTCA^+Cl$, 10 mmol of the alcohols and 30 % *aq.* H_2O_2 (15 mmol) at constant stirring and then heated to the required reaction temperature. Reaction products were characterized and quantified using GLC (Hewlett-Packard 5890 gas chromatograph with a flame ionization detector and 50 m X 0.32 mm 5 % phenyl methyl silicone capillary column and with N_2 carrier gas) where chlorobenzene was used as the internal reference. Products were also identified by GC-MS (Shimadzu Gas Chromatograph, GC-17A fitted with QP-500MS Mass Spectrometer) as well as with NMR spectroscopy.

2.3 Results and Discussions

2.3.1 Characterization of the catalysts

The elemental analysis results are plotted in table 1, 2 and 3 for $Na_9[SbW_9O_{33}].19.5H_2O$, $Na_{11}(NH_4)\{[Mn(H_2O)]_3(SbW_9O_{33})_2\}.45H_2O$ and $K_{12}\{[Zn(H_2O)]_3(SbW_9O_{33})_2\}.46H_2O$ respectively.

Thus it can be observed in the tables that the obtained elemental compositions agree well with the expected elemental compositions. Similarly the FT-IR bands agree with the literature values. The FT-IR spectra as KBr pellets are shown in Figure 1, 2 and 3 for $Na_9[SbW_9O_{33}].19.5H_2O$, $Na_{11}(NH_4)\{[Mn(H_2O)]_3(SbW_9O_{33})_2\}.45H_2O$ and $K_{12}\{[Zn(H_2O)]_3(SbW_9O_{33})_2\}.46H_2O$ respectively. The values are attributed as; (1) 934 cm⁻¹: $W=O_t$, (2) 865 cm⁻¹: $W-O_c-W$, (3) 772 cm⁻¹: $W-O_e-W$, where *t*: terminal oxygen atoms, *c*: corner sharing oxygen atoms and *e*: edge sharing oxygen atoms [18].

Hence, at this point it was confirmed that the desired compounds $Na_9[SbW_9O_{33}].19.5H_2O$, $Na_{11}(NH_4)\{[Mn(H_2O)]_3(SbW_9O_{33})_2\}.45H_2O$ and

$K_{12}\{[Zn(H_2O)]_3(SbW_9O_{33})_2\}.46H_2O$ have been formed and the same were studied as potential catalysts for the oxidation of a number of alkenes and alcohols.

Table 1: Elemental compositions obtained for $Na_9[SbW_9O_{33}].19.5H_2O$ compound

SL. No.	Element	Observed composition (%)	Expected composition (%)
1.	Na	7.14	7.23
2.	Sb	4.27	4.25
3.	W	57.67	57.80

Table 2: Elemental compositions obtained for $Na_{11}(NH_4)\{[Mn(H_2O)]_3(SbW_9O_{33})_2\}$. $45H_2O$ compound

SL. No.	Element	Observed composition (%)	Expected composition (%)
1.	Na	4.17	4.28
2.	Mn	2.69	2.78
3.	Sb	4.24	4.12
4.	W	55.79	55.99

Table 3: Elemental compositions obtained for $K_{12}\{[Zn(H_2O)]_3(SbW_9O_{33})_2\}.46H_2O$ compound

SL. No.	Element	Observed composition (%)	Expected composition (%)
1.	K	7.54	7.61
2.	Zn	3.21	3.19
3.	Sb	3.88	3.96
4.	W	53.71	53.84
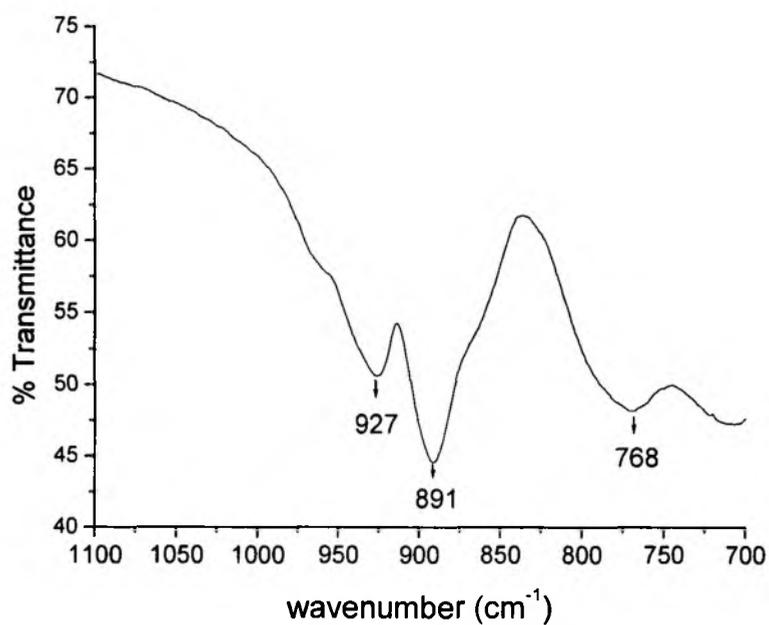
Figure 1: FT-IR spectrum of $Na_9[SbW_9O_{33}].19.5H_2O$ recorded as KBr pellet.
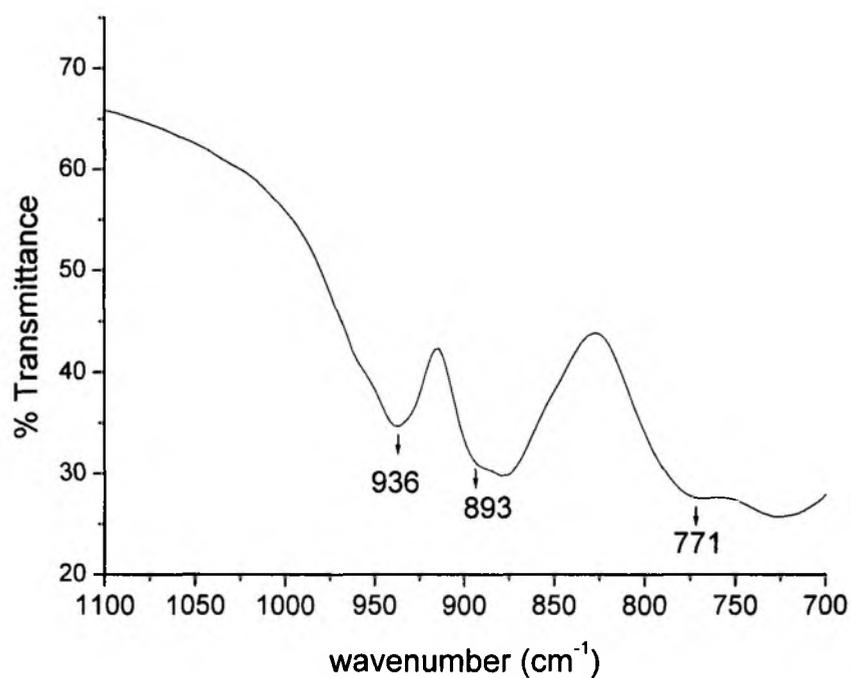
Figure 2: FT-IR spectrum of $Na_{11}(NH_4)\{[Mn(H_2O)]_3(SbW_9O_{33})_2\}.45H_2O$ recorded as KBr pellet.
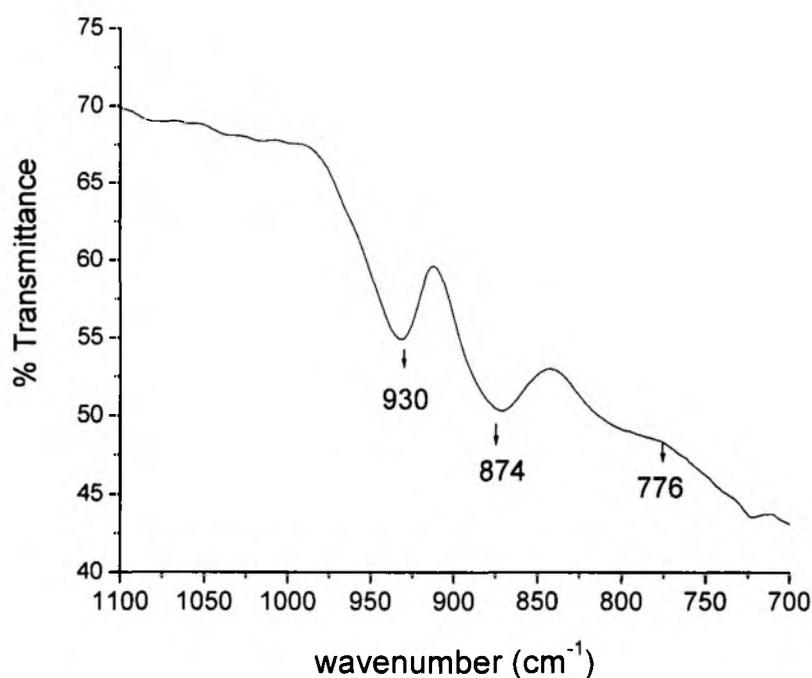
Figure 3: FT-IR spectrum of $K_{12}\{[Zn(H_2O)]_3(SbW_9O_{33})_2\}.46H_2O$ recorded as KBr pellet.

2.3.2. Catalytic studies

2.3.2.1 Catalytic activity of Na₁₁(NH₄){[Mn(H₂O)]₃(SbW₉O₃₃)₂}

The manganese ion substituted sandwich type polyoxotungstate $Na_{11}(NH_4)[Mn_3(H_2O)_3(SbW_9O_{33})_2]$, was subjected for making of its stock solution as seen in experimental section. The above stock solution was investigated for the epoxidation of limonene with aqueous hydrogen peroxide as the oxidant as seen in the experimental section. The reaction was carried out at 60°C and substrate: oxidant mole ratio was 1:2. The limonene conversion was 90% in 3 h of time interval. The only reaction product obtained was *cis* and *trans* isomers of limonene 1,2 epoxide in almost 1:1 ratio. The epoxidation in the case of limonene 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 results are given in Table 4.

Since manganese ions are the only species in the catalyst which can act as a redox centre, we thought of preparing analogous sandwich type polyoxometalates with other transition metal atoms like copper, cobalt and zinc. The copper and cobalt analogues were synthesized to see the individual activity of these metal ions and also to have a comparison of the same with the manganese ions. Similarly, since zinc is typically not a redox centre unlike manganese, copper or cobalt, it was chosen as a substitution towards some controlled reactions. Thus, the stock solutions of all these sandwich type polyoxotungstates were made and tested for limonene epoxidation, similar to the manganese ions substituted polyoxotungstate. The limonene epoxidation with all these polyoxotungstates were carried out and the results are given in table 4.

From the Table 4, it can be observed that the copper and cobalt based polyoxotungstates showed the same activity as their manganese analogue towards limonene epoxidation, both in terms of conversion and selectivity. Interestingly, even the zinc analogue gave similar conversion and selectivity values. This observation was really surprising as zinc has no redox center like manganese, copper or cobalt. Further studies clearly showed that the tungsten octahedral clusters are in fact the active centers for the epoxidation of alkenes, irrespective of whichever transition metal is present in the polyoxometalate framework. We observed that the magnitude 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. $K_{12}[Zn_3(H_2O)_3(SbW_9O_{33})_2].48H_2O$ was the same, and so was the activity of the capping agent $Na_9[SbW_9O_{33}].19.5H_2O$ itself. Based on the above observations, it was inferred that manganese ions may really not be the active centre, unlike what was concluded before. Thus we assumed that the tungstate species are really the active centers towards the epoxidation reactions and not the manganese species as was believed in the original article.

And to substantiate this point further, the $[MTCA]_9[SbW_9O_{33}]$ stock solution, which does not contain any other transition metal ion substitutions, was also tested as a catalyst for the same epoxidation. However, in order to maintain the number of tungsten atoms with respect to manganese or zinc based sandwich type polyoxotungstates, here twice the number of mols of precursor was taken as catalyst. Interestingly, the results were identical to that of manganese based catalysts i.e. $([MTCA]_{12}[Mn_3(SbW_9O_{33})_2]$. 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 of $[MTCA]_9[SbW_9O_{33}]$ in dichloroethane.

From the above results it was concluded that the tungsten octahedrons by themselves are active sites for the epoxidation with *aq.* H_2O_2 and there is no additional need of any transition metal atoms like manganese, cobalt or copper 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 prove yet another fact that the 'sandwich' structure is also not essential to demonstrate the catalytic activity for these polyoxotungstates. The typical structure of $[SbW_9O_{33}]^{9-}$ anion is shown in Figure 4 [18].

Table 4: Controlled experiments for oxidation of limonene using *aq.* H_2O_2

SL. No.	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	$[MTCA]_{12}[(Co_3(SbW_9O_{33})_2]$ in $C_2H_4Cl_2$	1000:1	92	3
3	$[MTCA]_{12}[(Cu_3(SbW_9O_{33})_2]$ in $C_2H_4Cl_2$	1000:1	89	3
4	$[MTCA]_{12}[(Zn_3(SbW_9O_{33})_2]$ in $C_2H_4Cl_2$	1000:1	91	3
5	$[MTCA]_9[SbW_9O_{33}]$ in $C_2H_4Cl_2$	500:1	92	3
6	$[MTCA]_9[BiW_9O_{33}]$ in $C_2H_4Cl_2$	500:1	90	3
7	$[MTCA]_8[TeW_9O_{33}]$ in $C_2H_4Cl_2$	500:1	91	3
8	$Na_9[SbW_9O_{33}]+ 9[MTCA]^+Cl^-$ in water	500:1	91	4
9	$Na_9[SbW_9O_{33}].19.5H_2O$	100:1	<1	6
10	$[MTCA]^+Cl^-$ in $C_2H_4Cl_2$	100:1	<1	6

Experimental condition: Temp: 60 °C, substrate: 30% *aq.* H_2O_2 (mol) was taken as 1:2. In all these cases, amounts of catalyst taken were based on the XW_9O_{33} unit content for a given amount of substrate (where X: Sb, Bi or Te).
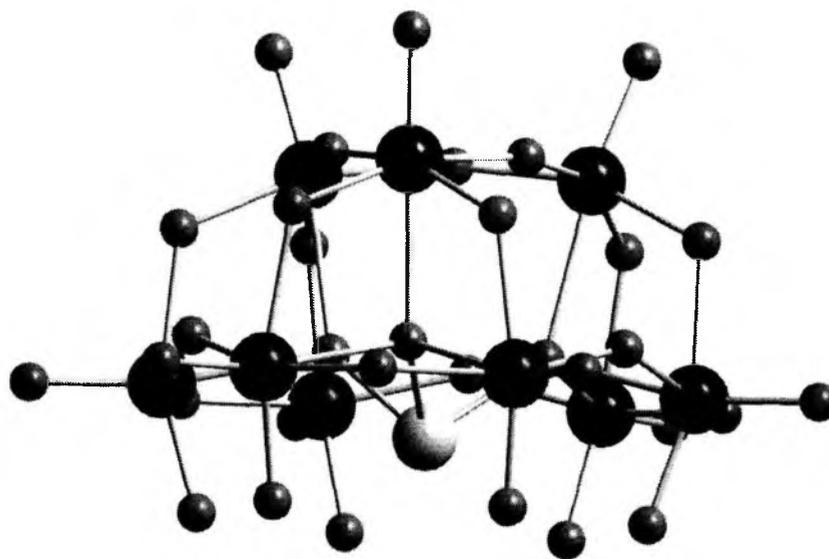
Figure 4: Ball and stick model of $[SbW_9O_{33}]^{9-}$ lacunary Keggin type polyoxometalate (Dark large circles: tungsten atoms, Light large circle: antimony atoms, Small circles: oxygen atoms) [18]

2.3.2.2 Effect of solvents on limonene epoxidation

The epoxidation reaction was tested in various solvents like dichloroethane, dichloromethane, chloroform, methanol, acetonitrile and acetone. The reaction worked successfully in water immiscible solvents like dichloroethane, dichloromethane or chloroform, but failed in hydrophilic solvents like acetone, methanol or acetonitrile. Thus it was realized that liquid-liquid biphasic medium is very essential for the catalytic system to demonstrate the activity. 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 can be seen in the experimental section. This reaction was also observed to have worked successfully as can be seen in table 4. It may be noted that similar to limonene, all the liquid alkenes used by us were typically immiscible with water under reaction conditions and hence the present system is always necessarily a liquid-liquid biphasic system. In case of solid alkenes like norbornene or *trans*-stilbene, small amount of water immiscible solvent like toluene (a non-halogenated solvent) was used for its dissolution. The purpose of selecting toluene was to avoid the use of halogenated

solvents that are proven to be toxic contaminants that have an adverse effect on the environment.

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 that is prepared separately. This retardation is because of the by-product NaCl that is formed on mixing $Na_9[SbW_9O_{33}]$ and $[MTCA]^+Cl^-$, as reported earlier by other groups [21]. Similar retardation was observed when 0.64 mol of NaCl was added to the reaction mixture, in which stock solution of $[MTCA][SbW_9O_{33}]$ was used as catalyst. Although the reactions decelerate, no decrease in the final conversion value was observed in the controlled experiments (Table 4).

2.3.2.3 Effect of temperature on limonene epoxidation

The rate of reactions increased with rise in the reaction temperature for all the alkenes. Figure 5 shows the typical trend for the epoxidation of limonene. Thus after 3 h of reaction interval only 41% conversion of limonene was observed at 35°C, however at 50 and 60°C it was 67 and 84% respectively for the same time interval (Figure 5). Accordingly, the energy of activation determined graphically was found to be 10.22 kcal K^{-1} mol^{-1} (Inset, Figure 6). The activation energy although low for catalytic reactions in general is quite typical for biphasic oxidation reactions [22]. Similarly, the values of the enthalpy of activation determined for limonene was 9.647 kcal K^{-1} mol^{-1}. As mentioned earlier 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 even at lower or higher temperatures indicating the catalytic system is highly efficient for regioselective epoxidation reactions of such dienes. Limonene-1,2-epoxide existed in both *cis* and *trans* isomeric forms in almost an equimolar ratio as can be seen in Figure 7.
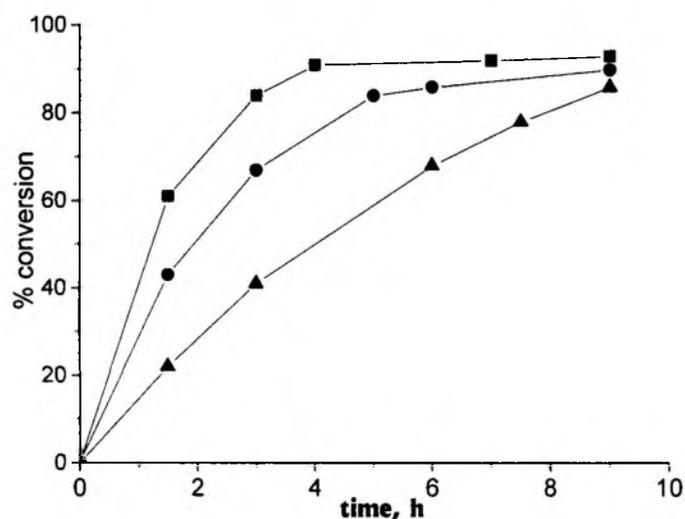
Figure 5: Kinetic plots of epoxidation of limonene over Na₉[SbW₉O₃₃] + 9 [MTCA]⁺Cl⁻ at different temperatures in the range 35 - 60 °C. Reaction conditions: Na₉[SbW₉O₃₃]: 0.01 mmol, [MTCA]⁺Cl⁻: 0.09 mmol, limonene: 5 mmol, 30% *aq.* H₂O₂: 10 mmol (▲: 35°C, ●: 50°C, ■: 60°C)
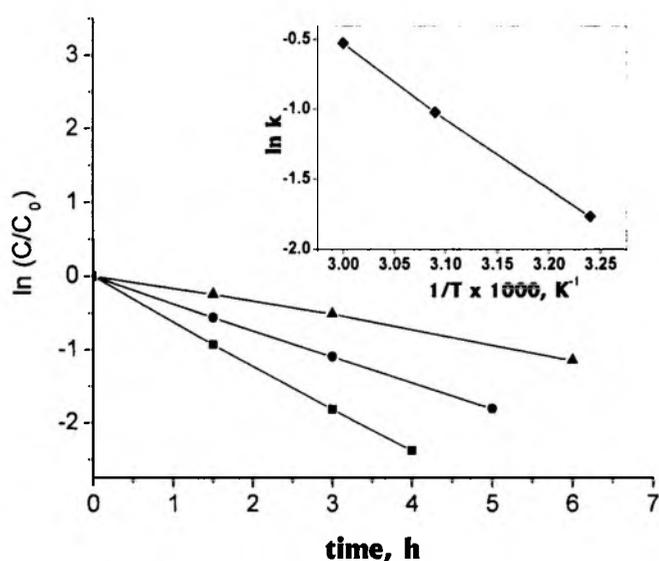
Figure 6: Kinetic profiles of limonene epoxidation reaction as a function of temperature and their linear fittings. *Reaction conditions:* Catalyst: 0.01 mmol, [MTCA]⁺Cl⁻: 0.09 mmol, limonene: 5 mmol, 30% *aq.* H₂O₂: 10 mmol (▲: 35°C, ●: 50°C, ■: 60°C). Inset: A plot of measured rate constants as a function of temperatures in an Arrhenius plot)
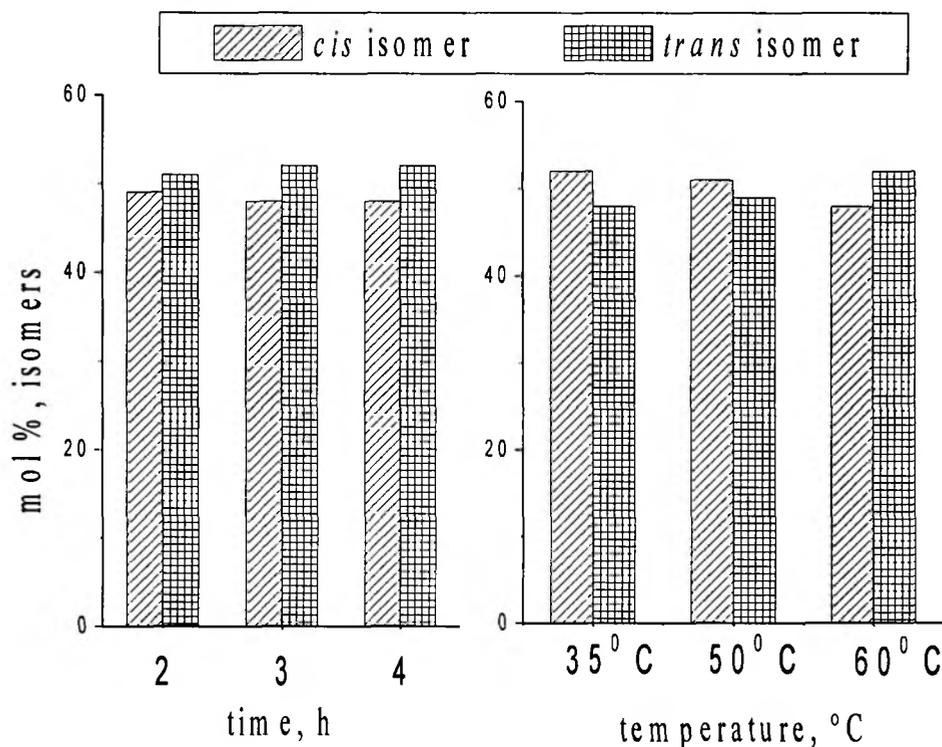
Figure 7: Selectivity of *cis* and *trans* isomers of Limonene 1, 2-epoxide:

    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% *aq.* H$_2$O$_2$: 10 mmol, Temp: 60^0 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 , 30% *aq.* H$_2$O$_2$: 10 mmol

2.3.2.4 Epoxidation of other alkenes

A variety of other alkenes *viz.* norbornene, cyclohexene, cyclooctene, *cis*-stilbene, *trans*-stilbene, styrene and 1-octene were also tested for the epoxidation studies. In the case of norbornene and cyclohexene, a lower substrate : oxidant ratio gave excellent selectivity for the epoxide as can be seen in Table 5. 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 [22]. 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 [23].

Terminal alkenes are normally very less reactive, but with the present 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.

Table 5: Oxidation of various alkenes over Na₉[SbW₉O₃₃]+9[MTCA]⁺Cl⁻ with *aq.* H₂O₂ as oxidant at different temperatures and different substrate: oxidant ratios

Substrate	Substrate: aq. H₂O₂	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)
Trans-stilbene [a]	1:2	60	9	17	Benzaldehyde (>99)
Styrene	1:2	60	6	73	Benzaldehyde (>99)
1-octene	1:2	60	9	38	1-octene epoxide (>99)

Reaction conditions: Na₉[SbW₉O₃₃]: 0.01 mmol, [MTCA]⁺Cl⁻: 0.09 mmol, Substrate: Catalyst Ratio : 500:1, [a] 1 ml toluene was used as solvent.

2.3.2.5 Oxidation of secondary and allylic alcohols
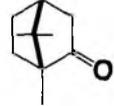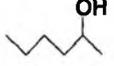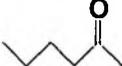
Having realized the activity of $Na_9[SbW_9O_{33}]$ in conjunction with a phase transfer catalyst, $MTCA^+Cl^-$ towards alkene epoxidation, the same was extrapolated towards the oxidation of a variety of secondary and allylic alcohols. The procedure for the same can be seen in experimental section. Although the catalyst showed some activity towards oxidation of secondary alcohols, it failed to show any activity towards the oxidation of primary alcohols; unless they were activated by an allylic or benzylic adjacency, as in the case of benzyl alcohol. In the case of secondary alcohols, the corresponding ketones was the only product, while in the case of allylic alcohol, the ketones, the epoxide and the epoxy-ketones were obtained, the major product being the ketone. Importantly, unlike alkenes, in the case of secondary as well as allylic alcohols the reaction had not slowed down on *in-situ* addition of $Na_9[SbW_9O_{33}]$ and $MTCA^+Cl^-$. Thus, the rate of reaction for *in-situ* addition of $Na_9[SbW_9O_{33}]$ and $MTCA^+Cl^-$ was same as that of addition of equimolar $Q_9[SbW_9O_{33}]$ stock solution, to the alcohol and hydrogen peroxide mixture.

In the case of secondary alcohols, oxidations of cyclic alcohols like cyclopentanol, cyclohexanol as well as *cis* and *trans*-isomers of methylated cyclohexanols were carried out, apart from linear alcohol like 2-hexanol. In all the cases near quantitative yields were obtained within two hours of reaction time. Structurally complex alcohols like borneol and menthol were also oxidized to corresponding ketones under the same condition and their yields were 87 and 93 % respectively. Benzylic and allylic alcohols also underwent a smooth oxidation to the corresponding aldehyde or ketones selectively, with this catalytic system. Oxidation of benzyl alcohol at 60 °C gave only 70 % conversion with more than 99 % selectivity to benzaldehyde after 5 h. However, at 80 °C the yield was above 94 % in 2 h. In the case of benzyl alcohol no noticeable benzoic acid was observed even at substrate: *aq.* H_2O_2 mol ratio of 1:1.5.

Linear allylic alcohols with terminal olefinic bond like 1-hexene-3-ol and 1-octene-3-ol were completely transformed into corresponding ketones with selectivity of more than 99 % at 80 °C in 3 and 2 h respectively with the current catalyst system. Similarly, in the case of cyclohexene-2-ol, cyclohexene-2-one was the only product with more than 99 % yield in 1 h at 80 °C. For 1-phenyl ethanol, the product yield was higher than 96 % in 1 h at 80 °C.
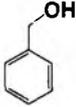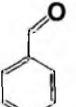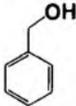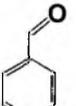
Turnover frequency (defined as moles of product found per mole of $Na_9[SbW_9O_{33}]$ per hour) approached >15000 h^{-1} for the oxidation of 1-phenyl ethanol when $Na_9[SbW_9O_{33}]$: substrate: *aq.* H_2O_2 mole ratio was 1:1,00,000:1,50,000 at 80 °C. The above re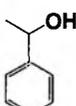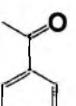sults show that $Na_9[SbW_9O_{33}]$ + $MTCA^+Cl^-$ catalyst system was very efficient and selective for oxidation of wide range of alcohols, in the absence of any solvents. The results for the oxidation studies of secondary alcohols can be seen in Table 6 and for the oxidation studies of allylic and benzylic alcohols can be seen in Table 7.

Table 6: Selective oxidation of secondary alcohols over Na$_9$(SbW$_9$O$_{33}$) + MTCA$^+$Cl$^-$ using *aq.* H$_2$O$_2$.

SL. No.	Substrate	Time, h	Product	Yield, %	TON
1	OH	2	O	93	930
2	OH (cis)	2	O	> 99	990
3	OH (trans)	2	O	95	950
4	OH (trans)	2	O	98	980
5	OH	2	O	> 99	990
6	OH	3	O	89	890
7	OH	3	O	97	970
8	OH	2	O	> 99	990
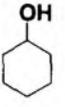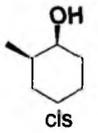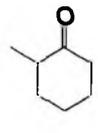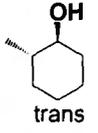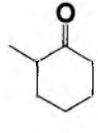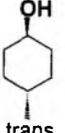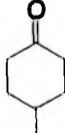
Reaction conditions: Na$_9$(SbW$_9$O$_{33}$): 0.01 mmol, MTCA$^+$Cl$^-$: 0.09 mmol, alcohols: 10 mmol, 30 % *aq.* H$_2$O$_2$: 15 mmol, temperature: 80 °C. Yields were determined by GC analysis based on alcohol conversion and selectivity to the product.

Table 7: Selective oxidation of benzylic and allylic alcohols over $Na_9(SbW_9O_{33})$ + $MTCA^+Cl^-$ using *aq.* H_2O_2

SL. No.	Substrate	Temp, °C	Time, h	Product	Yield, %	TON
1		60	5		70	700
2		80	2		94	940
3		60	2		83	830
4		80	1		96	960
5		80	1		68	990
6		80	1.5		72	990
7		80	1		78	990
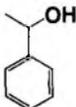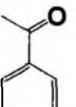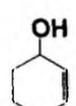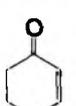
Reaction conditions: $Na_9(SbW_9O_{33})$: 0.01 mmol, $MTCA^+Cl^-$: 0.09 mmol, secondary alcohols: 10 mmol, 30 % *aq.* H_2O_2 : 15 mmol. Yields were determined by GC analysis based on alcohol conversion and selectivity to the product.

2.3.2.6 Effect of temperature on cyclohexanol oxidation

   Oxidation of cyclohexanol with *aq.* H_2O_2 over $Na_9[SbW_9O_{33}]$ + $MTCA^+Cl^-$ catalyst system was carried out with cyclohexanol: *aq.* H_2O_2 mol ratio of 1:1.5 in the temperature range 40-80 °C. Kinetics of the reaction were followed till maximum yield was obtained and the results are plotted in Figure 8. The cyclohexanol conversion and the reaction rate increase with increase in temperature without

affecting the selectivity of the required product, cyclohexanone. Accordingly, at 40 °C maximum conversion of ~ 74 % was obtained after 24 h whereas at 50 and 60 °C the cyclohexanol conversions were about 82 % after 8 and 5 h. However, at 80 °C maximum conversion of > 93 % was obtained within 2 h (Table 6).
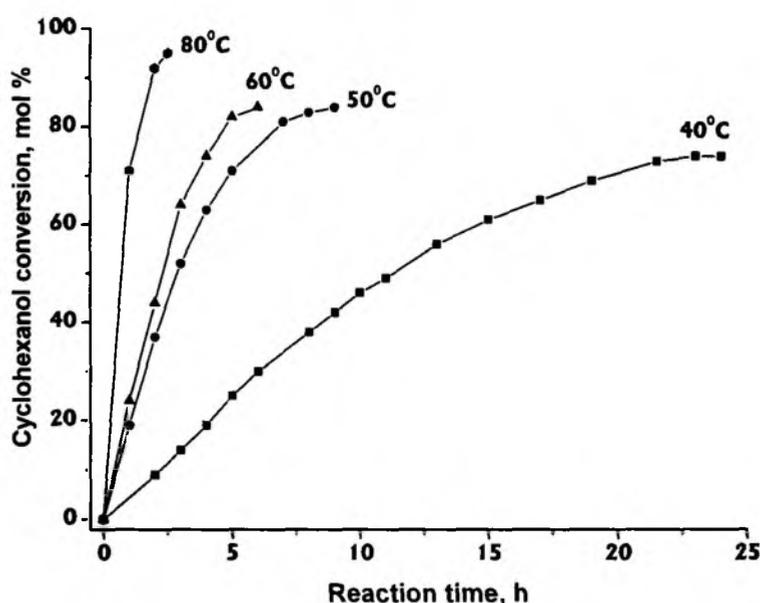
Figure 8: Kinetic plots of oxidation of cyclohexanol over $Na_9[SbW_9O_{33}]$ + 9 $MTCA^+Cl^-$at different temperatures in the range 40 - 80 °C. Reaction conditions: $Na_9[SbW_9O_{33}]$: 0.01 mmol, $MTCA^+Cl^-$: 0.09 mmol, alcohol: 10 mmol, 30 % *aq.* H_2O_2: 15 mmol

Kinetic measurements for cyclohexanol oxidation reaction were carried at as a function of temperature and the results are plotted in Figure 9 and the data showed the reaction to be first order with respect to cyclohexanol. The rate constants at different reaction temperatures between 40 and 60°C were obtained by subjecting the data to linear regression as shown in the figure. Arrhenius equation was used with the above rate constant data to estimate the activation parameters for the cyclohexanol oxidation reaction (inset in Figure 9). The Energy of activation was obtained as 15.57 kcal/mol while the Enthalpy of activation was 10.2 kcal/mol. The obtained activation energy is typical for biphasic oxidation as observed in the literature, and as also seen above in the case of alkenes [22].
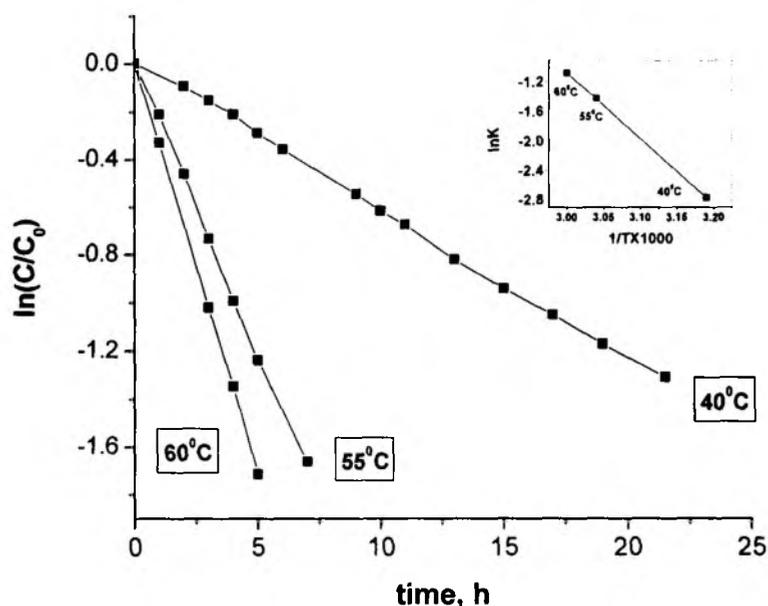
Figure 9: Kinetic profiles of cyclohexanol oxidation reaction as a function of temperature and their linear fitting. Reaction condition: catalyst: 0.01 mmol, MTCA$^+$Cl$^-$: 0.09 mmol, alcohol: 10 mmol, 30% *aq.* H₂O₂: 15 mmol. Inset: a plot of the measured rate constants as a function of temperatures in an Arrhenius plot

2.3.2.7 Effect of substrate: oxidant ratio on cyclohexanol oxidation

In an attempt to optimize the amount of *aq.* H₂O₂ needed for cyclohexanol oxidation reaction, *experiments* were carried out with different cyclohexanol: *aq.* H₂O₂ mol ratios at 60 °C and results are plotted in Figure 10. With cyclohexanol: H₂O₂ mole ratio of 1:0.5 and 1:1 the conversions were 30 and 39 % respectively and no further increase in the conversion observed thereafter. With cyclohexanol: H₂O₂ mol ratio of 1:1.5 the conversion was as high as 84 % after 6 h and for 1:2 mol ratio, the cyclohexanol conversion was almost the same as that of 1:1.5 ratio, indicating that the substrate: *aq.* H₂O₂ mol ratio of 1:1.5 was optimum to obtain a satisfactory yield with the current catalytic system. Thus, the substrate: *aq.* H₂O₂ mol ratio of 1:1.5 was employed in all further reactions.
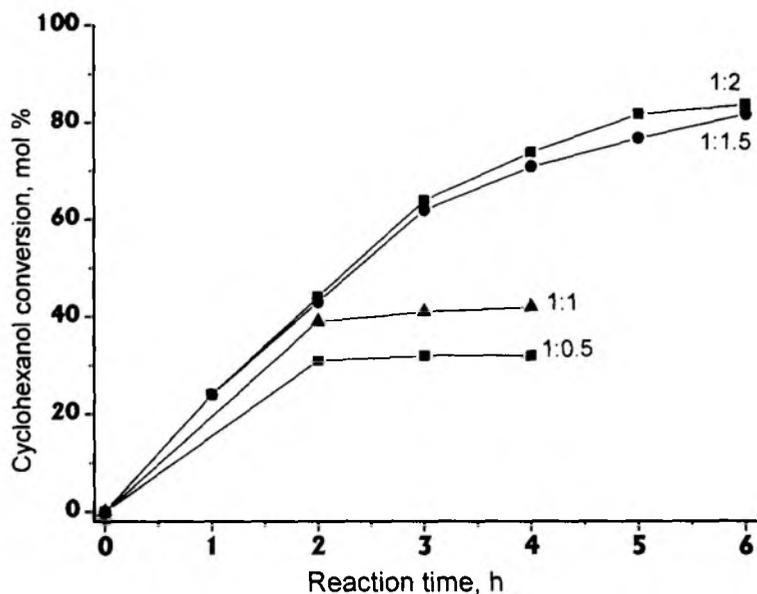
Figure 10: Oxidation of cyclohexanol over Na₉[SbW₉O₃₃] + 9 MTCA⁺Cl⁻ with different substrate : *aq.* H₂O₂ ratio. *Reaction conditions*: Na₉[SbW₉O₃₃]: 0.01 mmol, MTCA⁺Cl⁻: 0.09 mmol, alcohol: 10 mmol, temperature: 60 °C

In an attempt to see whether multiple fractional addition of *aq.* H₂O₂ to substrates with certain time intervals is of any advantage over a single addition of the whole amount of *aq.* H₂O₂, experiments with addition of 1.5 mole equivalent of *aq.* H₂O₂ in one lot as well as in multiple fractional additions were carried out at 60 °C over the present catalyst system for cyclohexanol oxidation reaction and the results are shown in Figure 11. As seen in the figure, the total conversion of cyclohexanol, thus the yield of the cyclohexanone, was nearly the same whether the addition of 1.5 mol equivalent of *aq.* H₂O₂ was added in one lot or multiple fractions. In fact multiple fractional additions require more time than that required for one lot addition to achieve the same conversion as seen in the figure. Thus, addition of total amount of the oxidant was done in one lot for all other reactions.
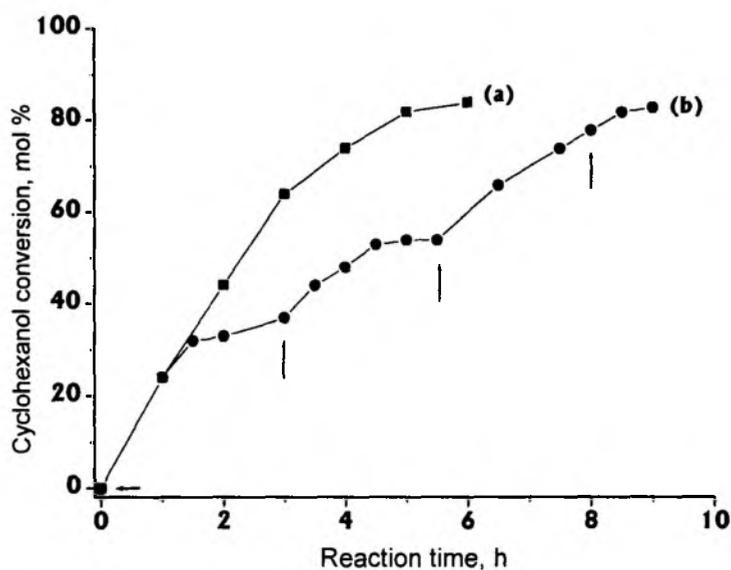
Figure 11: Oxidation of cyclohexanol over $Na_9[SbW_9O_{33}]$ + 9 $MTCA^+Cl^-$ with (a) one-lot addition and (b) fractional additional (3 X 0.5 mol) of 1.5 mol *aq.* H_2O_2 equivalent of with reference to cyclohexanol. Reaction conditions: catalyst: 0.01 mmol, $MTCA^+Cl^-$: 0.09 mmol, alcohol: 10 mmol, temperature: 60 °C. ↑ indicates the time when 0.5 mol fraction of *aq.* H_2O_2 added

### 2.3.3 Active center of the catalyst and reaction mechanism

UV-visible studies were conducted for the separated and well-dried dichloroethane solutions of manganese containing polyoxotungstate (Figure 12, left) and the antimony based precursor (Figure 12, right) before and after interaction with aq H_2O_2. The spectra of both the polyoxotungstates before interaction with H_2O_2 were identical, which changed after with the addition of H_2O_2 in both the cases. However, the spectra of both the polyoxotungstates on treating with H_2O_2 were also identical to each other. The bands seen in the UV region correspond to [MTCA] group [18]. Upon interaction with H_2O_2, shifts in bands are observed due to changes in the environment of these anions. This indicates that the changes that are taking place in manganese containing polyoxotungstate are also occurring in the antimony based capping agent.
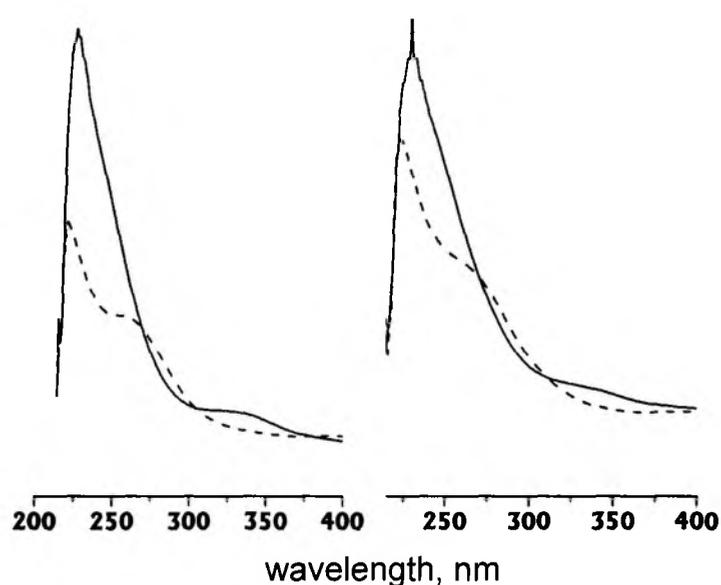
Figure 12: UV-visible spectra of [MTCA]$_9$[SbW$_9$O$_{33}$] (left) and [MTCA]$_{12}$ [Mn$_3$(SbW$_9$O$_{33}$)$_2$] (right) in 1, 2 dichloroethane (Dashed lines: before interaction with 30% *aq.* H$_2$O$_2$, Solid lines: after interaction with 30% *aq.* H$_2$O$_2$)

However, UV-visible spectra were not adequate in explaining the mechanism of reaction, thus IR spectroscopy was used as a probe to investigate the nature of active peroxo species, as well as to study the stability of the catalyst under the experimental conditions [22]. Due to the limitation of IR measurement with aqueous solution, IR measurements were made with the dichloroethane solution of [MTCA]$_9$[SbW$_9$O$_{33}$] on KBr discs before and after treating with *aq.* H$_2$O$_2$ and the spectra can be seen in Figure 13 (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: corner sharing, e: edge sharing). An additional peak appearing at 834 cm^{-1} after the above solution was treated with *aq.* H$_2$O$_2$, is attributed to the formation of tungsten-peroxo species in accordance with the literature [22]. On treatment with 10% *aq.* KI, the peroxide decomposes and the peak at 834cm^{-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$_9$O$_{33}$)$_2$] and the spectra were identical to [MTCA]$_9$[SbW$_9$O$_{33}$] spectra (Figure 13, 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$_9$O$_{33}$] in dichloroethane solvent became futile. However, number of peroxo species formed was estimated to be six per unit of [SbW$_9$O$_{33}$] by titration between dichloroethane solutions of the peroxo intermediate complexes with methanolic Ce (IV) [24].


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Wavenumber, cm^{-1}
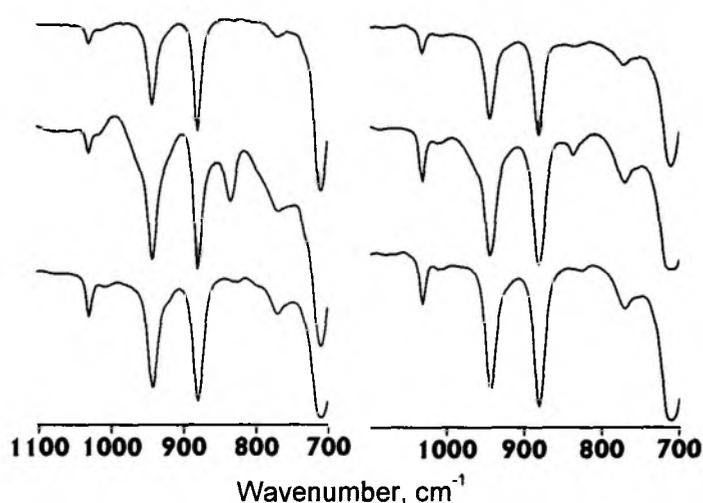
Figure 13: FT-IR spectra of [MTCA]$_9$[SbW$_9$O$_{33}$] (left) and [MTCA]$_{12}$[Mn$_3$(SbW$_9$O$_{33}$)$_2$] (right) in 1, 2 dichloroethane (Top: before reaction, Center: after addition of 30% *aq.* H$_2$O$_2$, Bottom: after decomposition of excess of peroxide with 10% KI solution)

Finally, on the basis of IR observations a model of the reaction mechanistic pathway for the epoxidation of alkenes (Scheme 1) or oxidation of alcohols (Scheme 2) is proposed. One or more tungstate octahedron of the Na$_9$[SbW$_9$O$_{33}$] cluster bind to peroxo species with possible seven coordination and the original structure is retained on the completion of oxidation reaction.
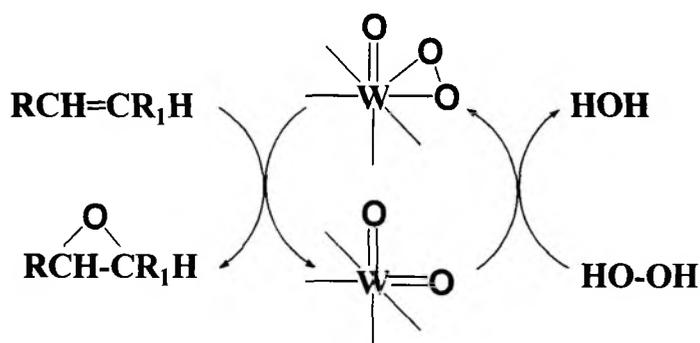
Scheme: 1 Proposed model for reaction mechanism for epoxidation of alkenes
(Only single tungsten octahedra is shown for clarity)
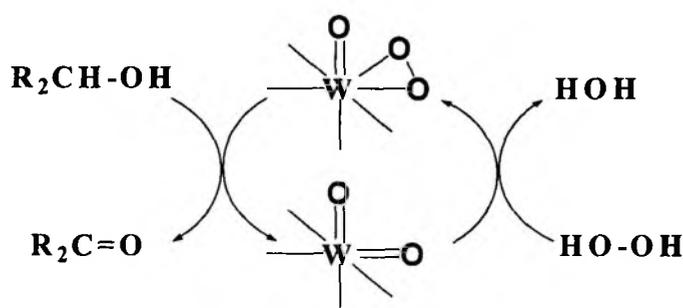
Scheme: 2 Proposed model for reaction mechanism for oxidation of alcohols
(Only single tungsten octahedra is shown for clarity)

2.4 Summary and Conclusion

The results clearly indicate that $Na_9[SbW_9O_{33}]$ in conjunction with a phase transfer catalyst $[MTCA]^+Cl^-$ is capable of selectively oxidizing a number of structurally different alkenes as well as a variety of secondary and allylic in high yields. In most of the cases the selectivity for epoxide (in the case of alkenes) or ketone (in the case of alcohols) was excellent. Importantly, there is no need of any solvent for the reaction (except when the substrate 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 *aq.* 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 *aq.* H_2O_2 was used as the oxidant.

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