[SbW$_9$O$_{33}$]-based polyoxometalate combined with a phase transfer catalyst: A highly effective catalyst system for selective oxidation of alcohols with H$_2$O$_2$, and spectroscopic investigation

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Abstract

Na$_9$[SbW$_9$O$_{33}$] in conjunction with a phase transfer catalyst, methyltricapryl ammonium chloride, is highly efficient for selective oxidation of variety of alcohols with aq. H$_2$O$_2$ to yield corresponding carbonyls. Most importantly the reactions are carried out in the absence of any organic solvents especially halogenated solvents. In case of allylic alcohols, the catalyst is highly selective for the alcohol oxidation reaction and least selective for epoxidation reaction in the presence of aq. H$_2$O$_2$. IR studies support the formation of W-peroxo intermediate species and also support the stability of the catalyst in the presence of phase transfer compound under the present experimental condition. The catalyst can be reused after careful decomposition of peroxide of the final reaction mixture.

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1. Introduction

Selective oxidation of alcohols to their carbonyls is of paramount importance in organic synthesis [1,2]. Generally, these reactions involve stoichiometric quantities of inorganic/organic oxidants [3], toxic or hazardous oxidizing agents [4,5]. However, from the environmental point of view oxidation reactions with green oxidants like O$_2$ or H$_2$O$_2$ are desirable. It is also highly desirable that the catalyst is stable and active under the experimental condition as many organo-metallic compound-based catalysts which are used for oxidation reactions, are vulnerable to decomposition due to oxidation of organic parts of the compounds.

There have been many reports in recent years for oxidation of alcohols using molecular oxygen and H$_2$O$_2$ as oxidants [6–17]. For the usage of H$_2$O$_2$ as an oxidant, transition metal ions based catalysts with d^0 electronic configuration, for example, Mo(VI) and W(VI), were found to be most effective for alcohol oxidation reactions, possibly due to their poor activity for H$_2$O$_2$ dismutation reaction [13–17]. Noyori and group used Na$_2$WO$_4$ in conjunction with a special phase transfer catalyst bearing

HSO$_4$ group as efficient catalytic system for oxidation of several alcohols at 90 °C [18], where the phase transfer catalyst was synthesized from tri-*n*-octylamine, dimethyl sulphate and sulphuric acid, but with a low yield [19,20]. Moreover, Na$_2$WO$_4$ based catalytic system is least active with a commonly available phase transfer catalyst like tetrabutyl ammonium halides or methyltricapryl ammonium chloride [18].

Among Mo and W-based catalysts, transition metal ions substituted sandwich type-polyoxometalates have attracted a great attention in recent years as they are oxidatively and solvolytically more stable than the conventional Keggin type polyoxometalates and metalloporphyrins [21–29]. In addition, the advantage of polyoxometalates as catalysts is that they are easy to synthesize as compared to zeolites or molecular sieves. Most of the known polyoxometalate based catalysts were used as homogeneous catalysts with halogenated solvents, and their reusability and the nature of reaction intermediate species responsible for the oxidation reactions are not unambiguously clear. Thus, our interest of the present work is to identify simple and efficient catalyst system, especially polyoxotungstate based catalysts, for oxidation of wide range of alcohols using a clean oxidant especially under solvent-free condition and also to identify the active center/species responsible for the oxidation reaction with aq. H$_2$O$_2$.

Here, we report Na$_9$[SbW$_9$O$_{33}$] in conjunction with a commonly available phase transfer compound, methyltricapryl

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ammonium chloride (MTCA$^+$Cl$^-$), as a highly efficient catalyst system for selective oxidation of alcohols with aq. H$_2$O$_2$ to their corresponding carbonyls. We have also found that the catalyst system has high tolerance for wide range of alcohols. Selective oxidation of several secondary alcohols, benzylic and allylic alcohols were investigated in the absence of any organic solvents especially halogenated solvents.

2. Experimental

2.1. Materials

Sodium tungstate dihydrate and Sb$_2$O$_3$ were purchased from Loba Chemie, India. Aq. H$_2$O$_2$ (30%) was purchased from Merck and exact strength at the time of usage was estimated by iodometric titration. Substrates used were of highest purity purchased from Aldrich. Aliquat 336 (methyl tricapryl ammonium chloride), dichloroethane 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. 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 (Perkin-Elmer Plasma 1000 Emission Spectrometer) for Na, Sb, Zn and Mn, 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$_9$O$_{33}$] was prepared as per the reported literature [30,31] and their structures were confirmed by IR and elemental analysis. [MTCA]$_9$[SbW$_9$O$_{33}$] was prepared by exchanging the sodium ions of Na$_9$[SbW$_9$O$_{33}$] with MTCA$^+$Cl$^-$ and then extracted into C$_2$H$_4$Cl$_2$ layer [30]. Sodium content of the above solution (as analyzed by ICP) below detection limit (0.1 ppm) indicating that the possibility for partially exchanged Na$_x$[MTCA]$_{9-x}$[SbW$_9$O$_{33}$] species can be ruled out.

In a typical catalytic reaction, a 25 ml two-necked round bottom flask equipped with a condenser was charged with 0.01 mol of Na$_9$[SbW$_9$O$_{33}$] and 0.09 mol of MTCA$^+$Cl$^-$, 10 mmol of alcohol and 15 mmol of 30% aq. H$_2$O$_2$ at constant stirring and then heated to the required temperature. It may be noted here that alcohols used here are immiscible with water at reaction condition and hence the present system necessarily involves two phases. The catalyst will initially be in the aqueous phase but under the virtue of Aliquat, it is pulled into the organic layer. No precipitated catalyst, either partly or largely, was noticed. Reaction products were characterized and quantified using GC (Hewlett-Packard 5890 gas chromatograph with a flame ionization detector and 50 m × 0.32 mm 5% phenyl methylsilicone

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).

3. Results and discussion

3.1. Oxidation of alcohols

Na$_9$[SbW$_9$O$_{33}$] in conjunction with a phase transfer compound, MTCA$^+$Cl$^-$, was used as a catalyst system for oxidation of variety of alcohols using aq. H$_2$O$_2$ as an oxidant. Detailed catalytic experiments and other spectroscopic studies are given here only for the oxidation of cyclohexanol, while for all other alcohols the end results are discussed. Oxidation of cyclohexanol with aq. H$_2$O$_2$ over Na$_9$[SbW$_9$O$_{33}$] + MTCA$^+$Cl$^-$ catalyst system was carried out with cyclohexanol:aq. H$_2$O$_2$ mol ratio of 1:1.5 in the temperature range 40–80 °C. Kinetics of the reaction were followed until maximum yield was obtained and the results are plotted in Fig. 1. The cyclohexanol conversion increases with increase in temperature. Accordingly, at 40 °C maximum the cyclohexanol conversion of ∼74% was obtained after 24 h whereas at 55 and 60 °C the cyclohexanol conversions were about 83 and 84% after 8 and 5 h, respectively. However, at 80 °C maximum conversion of >93% was achieved within 2 h (see Table 1). Interestingly, cyclohexanone was the only product in the above reactions [32].

Kinetic measurements for cyclohexanol oxidation reaction were carried at as a function of temperature and the results are plotted in Fig. 2 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 figure in Fig. 2). The parameters obtained were: the activation energy: 17.74 ± 0.14 kcal/mol, $\Delta H_{298}^{\ddagger}$: 10.2 ± 0.14 kcal/mol, $\Delta S_{298}^{\ddagger}$: 10.2 ± 0.14 kcal/mol. The
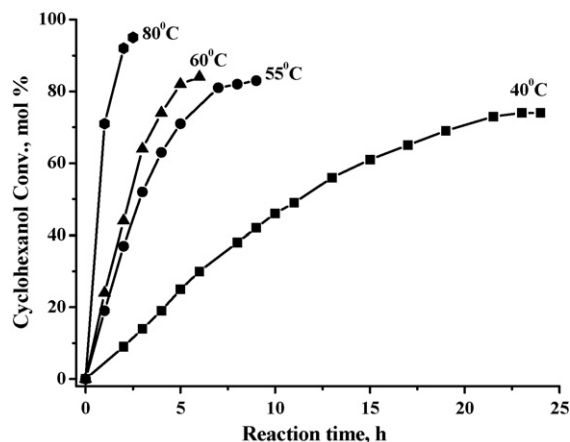
Fig. 1. Kinetic plots of oxidation of cyclohexanol over Na$_9$[SbW$_9$O$_{33}$] + 9 MTCA$^+$Cl$^-$ at different temperatures in the range 40–80 °C. Cyclohexanone was the only product. *Reaction condition*—catalyst: 0.01 mmol, methyltricaprylammonium chloride: 0.09 mmol, alcohol: 10 mmol, 30% aq. H$_2$O$_2$: 15 mmol.

Table 1
Selective oxidation of alcohols over $Na_9(SbW_9O_{33}) + MTCA^+Cl^-$ using aq. H_2O_2

S. no.	Substrate	Time (h)	Product	Yield (%)	TON
1		2		93	930
2	cis	2		>99	990
3	trans	2		95	950
4	cis	2		96	960
5	trans	2		98	980
6		2		>99	990
7		3		89	890
8		3		97	970
9		2		>99	990

Reaction condition—$Na_9(SbW_9O_{33})$: 0.01 mmol, $MTCA^+Cl^-$: 0.09 mmol, alcohol: 10 mmol, 30% aq. H_2O_2: 15 mmol, temperature: 80 °C. Yields were determined by GC analysis based on alcohol conversion and the product selectivity. In case of menthol and borneol, 1 ml of toluene was used for dissolution.

obtained activation energy is typical for biphasic oxidation as observed in the literature [16].

In an attempt to optimize the amount of aq. H_2O_2 needed for maximum cyclohexanol conversion, experiments were carried out with different cyclohexanol:aq. H_2O_2 mol ratios at 60 °C and results are plotted in Fig. 3. With cyclohexanol:aq. H_2O_2 mol ratio of 1:0.5 and 1:1, maximum conversions were 30 and 35%, respectively. With cyclohexanol:H_2O_2 mol ratio of 1:1.5 the conversion was 84% after 6 h and with 1:2 mol ratio, the cyclohexanol conversion was nearly the same as that of 1:1.5 ratio, indicating that the cyclohexanol:aq. H_2O_2 mol ratio of 1:1.5 was optimum to obtain a satisfactory yield with the current catalytic system. Thus, the substrate:aq. H_2O_2 mol ratio of 1:1.5 was employed in all further reactions.
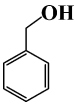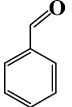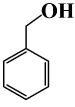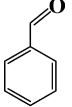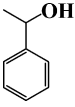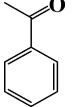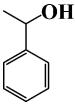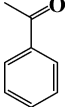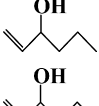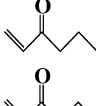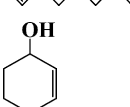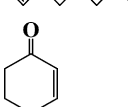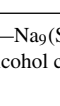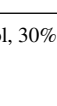
Another attempt was made to see whether multiple fractional addition of aq. H_2O_2 to cyclohexanol with certain time intervals is of any advantage over a single addition of the whole amount of aq. H_2O_2. Accordingly, experiments were carried out

at 60 °C where 1.5 mol equivalent of aq. H_2O_2 was added to cyclohexanol in one lot as well as in multiple fractional additions (3 mol × 0.5 mol) and the results are shown in Fig. 4. 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. H_2O_2 was added in one lot or in multiple fractions. In fact, multiple fractional additions required more time to achieve the same conversion. Thus, addition of total amount of aq. H_2O_2 was done in one lot for all other reactions.

Apart from cyclohexanol, oxidation of other cyclic alcohols like *cis* and *trans*-isomers of methylated cyclohexanols and cyclopentanol, as well as linear alcohol like 2-hexanol were also carried out over $Na_9[SbW_9O_{33}] + MTCA^+Cl^-$ catalyst system with substrate:aq. H_2O_2 ratios of 1:1.5 at 80 °C. In all the cases near quantitative yields were obtained within 2 h of reaction time (Table 1). Borneol and menthol (Table 1, entries 7 and 8) were also oxidized to corresponding ketones under the same condi-

Table 2
Selective oxidation of benzylic and allylic alcohols over $Na_9(SbW_9O_{33}) + MTCA^+Cl^-$ using aq. H_2O_2

S. no.	Substrate	Temperature (°C)	Time (h)	Product	Yield (%)	TON
1	OH (benzyl alcohol)	60	5	CHO (benzaldehyde)	70	700
2	OH (benzyl alcohol)	80	2	CHO (benzaldehyde)	94	940
3	OH (1-phenyl ethanol)	60	2	acetophenone	83	830
4	OH (1-phenyl ethanol)	80	1	acetophenone	96	960
5	OH	80	1.5	O	68	990
6	OH	80	1	O	72	990
7	OH (cyclohexenol)	80	1	O (cyclohexenone)	78	990

Reaction condition—$Na_9(SbW_9O_{33})$: 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 the product selectivity.

tion and their yields were 87 and 93%, respectively. Benzylic and allylic alcohols also underwent a facile oxidation to the corresponding aldehyde/ketones with high selectivity over the present catalytic system and the results are shown in Table 2. Oxidation of benzyl alcohol at 60 °C gave 70% conversion with more than 99% selectivity to benzaldehyde after 5 h. At 80 °C

with the same selectivity, the conversion was >93% in 2 h. It may be noted here that no trace of benzoic acid was found even at benzyl alcohol:aq. H_2O_2 mol ratio of 1:1.5 with the present catalyst system unlike with the reported catalytic systems [18]. With 1-phenyl ethanol, the product yield was higher than 96% in 1 h at 80 °C.

Generally olefinic bonds in allylic alcohols are reactive particularly to epoxidation apart from alcohol oxidation reaction resulting in unselective products with most of the reported cat-
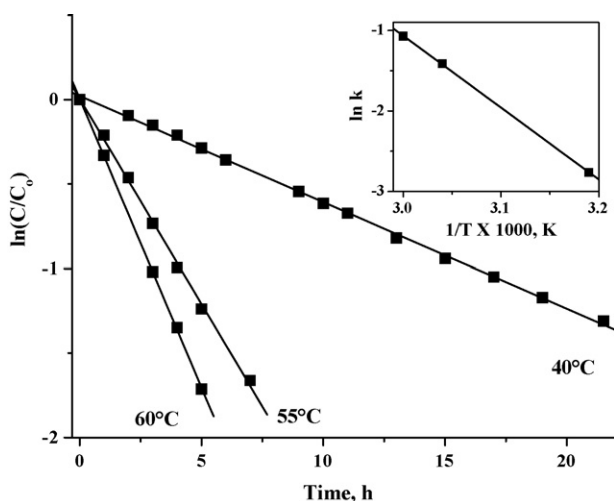
Fig. 2. Kinetic profiles of cyclohexanol oxidation reaction as a function of temperature and their linear fitting. *Reaction condition*—catalyst: 0.01 mmol, methyltricaprylammonium chloride: 0.09 mmol, alcohol: 10 mmol, 30% aq. H_2O_2: 15 mmol. Inset: a plot of the measured rate constants as a function of temperatures in an Arrhenius plot.
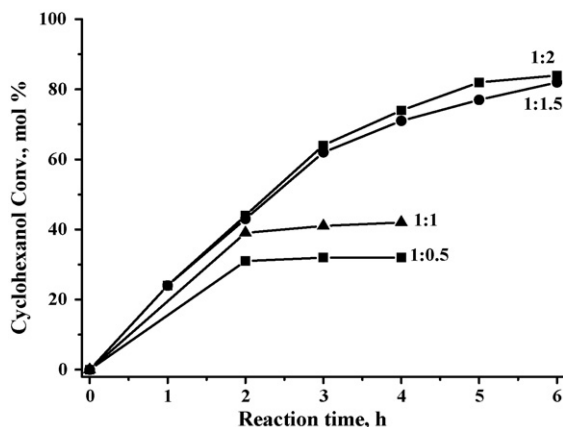
Fig. 3. Oxidation of cyclohexanol over $Na_9[SbW_9O_{33}] + 9\ MTCA^+Cl^-$ with different cyclohexanol:aq. H_2O_2 ratio. *Reaction condition*—catalyst: 0.01 mmol, methyltricaprylammonium chloride: 0.09 mmol, alcohol: 10 mmol, temperature: 60 °C.
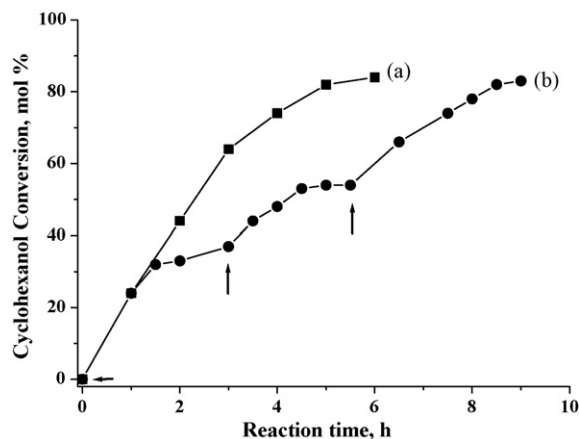
Fig. 4. Oxidation of cyclohexanol over $Na_9[SbW_9O_{33}] + 9$ $MTCA^+Cl^-$ with (a) one-lot addition of 1.5 mol and (b) fractional additional of 1.5 mol (3 mol × 0.5 mol) equivalent of aq. H_2O_2 to cyclohexanol. *Reaction condition*—catalyst: 0.01 mmol, methyltricaprylammonium chloride: 0.09 mmol, alcohol: 10 mmol, temperature: 60 °C. ↑ indicates the time when 0.5 mol fraction of aq. H_2O_2 added.

alyst systems in the presence of aq. H_2O_2 [17,18]. Oxidation of linear allylic alcohols with terminal olefinic bond like 1-hexene-3-ol and 1-octene-3-ol, were carried out over the current catalyst system and near quantitative conversion was achieved in 90 and 60 min, respectively with major products were corresponding ketones (68 and 72%, respectively). The side products were epoxy alcohol (8 mol%) and epoxy ketone (24 mol%) in case of 1-hexene-3-ol oxidation, and in the case of 1-octene-3-ol the products were epoxy alcohol with 8 mol%, and epoxy ketone with 20 mol% selectivity. Similarly, in case of cyclohexene-2-ol oxidation, nearly quantitative conversion was achieved in 1 h at 80 °C with 78 mol% product selectivity to cyclohexene-2-one and 22 mol% selectivity to epoxy cyclohexanol (Table 2). It may be noted here that even with the catalyst system like $Na_2WO_4 + [CH_3(n-C_8H_{17})_3N]HSO_4$, the oxidation of a linear allylic alcohol containing terminal olefinic bond the required carbonyl product was reported to be contaminated with considerable amount of epoxide [18].

Turnover frequency (TOF, h^{-1}), defined as moles of product formed per mol of $Na_9[SbW_9O_{33}]$ per hour, was approached >15,000 h^{-1} for the oxidation of 1-phenyl ethanol when $Na_9[SbW_9O_{33}]$:aq. H_2O_2:substrate mol ratio of 1:150,000:100,000 was used at 80 °C. Thus, the above results indicate that $Na_9[SbW_9O_{33}] + MTCA^+Cl^-$ catalyst system was highly efficient and selective for oxidation of wide range of alcohols. It is important to note here that no organic solvents were employed for the oxidation reactions, whereas most of the reported polyoxometalate catalysts for oxidation/epoxidation reactions employ halogenated solvents [8,13,16,30].

3.2. Active center of the catalyst and reaction mechanism

In cases of the transition metal ions substituted sandwiched polyoxotungstate based catalysts, it has been believed that either W center or cooperative effect between the W center and substituted transition metal ions which are sandwiched between two
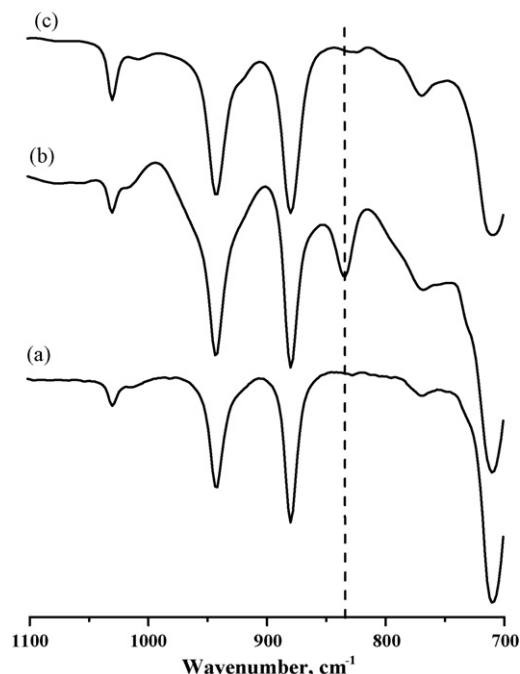

Fig. 5. IR spectra of $[MTCA]_9[SbW_9O_{33}]$ in $C_2H_4Cl_2$: (a) before reaction, (b) after addition of 30% H_2O_2 and (c) after decomposition of excess of H_2O_2 with KI solution.

lacunary tungstate clusters are responsible for oxidation reactions with hydrogen peroxide [16,30]. Infra red spectroscopy was used to probe the nature of active peroxo species with the present catalytic system, where there is no extra transition metal ion substitution, responsible for the selective oxidation reactions. Due to the limitation of IR measurement with aqueous solution, the measurements were made with $C_2H_4Cl_2$ solution of $[MTCA]_9[SbW_9O_{33}]$ on KBr disc before and after treating with aq. H_2O_2 ($C_2H_4Cl_2$ solution of $[MTCA]_9[SbW_9O_{33}]$ was interacted with aq. H_2O_2 for 30 min with vigorous stirring at 60 °C and then separated from the aqueous medium) and the resultant spectra are given in Fig. 5. It may be noted here that oxidation result of cyclohexanol with $[MTCA]_9[SbW_9O_{33}]$ catalyst in $C_2H_4Cl_2$ was almost the same as that of the reaction with $Na_9[SbW_9O_{33}] + 9$ $MTCA^+Cl^-$ in aqueous medium (Table 3). The IR peaks were 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 at 834 cm^{-1} appeared after reacting $[MTCA]_9[SbW_9O_{33}]$ with aq. H_2O_2 is attributed to the formation of W-peroxo species which is in accordance with the literature [16]. On treatment with 10% aq. KI which decomposes the peroxide species, the peak at 834 cm^{-1} disappeared and the resultant spectrum was identical to that of the fresh $[MTCA]_9[SbW_9O_{33}]$ (Fig. 5). The above results clearly indicate that W-peroxo species was the possible intermediate species involved in the selective oxidation of alcohols as proposed in Scheme 1. The W-peroxo might probably have been formed via hydroxy-hydroperoxo species. Efforts made to isolate the peroxo intermediate presumably formed during the hydrogen peroxide treatment with $[MTCA]_9[SbW_9O_{33}]$ in dichloroethane solvent became futile. However, number of

Table 3
Controlled experiments on oxidation of cyclohexanol using aq. H_2O_2

Entry	Catalyst	Oxidant	Yield (mol%)
1	$Na_9[SbW_9O_{33}] + 9$ $MTCA^+Cl^-$ in H_2O	Aq. H_2O_2	93
2	$[MTCA]_9[SbW_9O_{33}]$ in CH_2Cl_2	Aq. H_2O_2	91
3	$Na_9[SbW_9O_{33}] + 9$ $MTCA^+Cl^-$ in H_2O	Air	<1
4	$MTCA^+Cl^-$	Aq. H_2O_2	0
5[a]	$Na_9[SbW_9O_{33}]$	Aq. H_2O_2	<10

Experimental condition—temperature: 80 °C, time: 2 h. In all these cases, amounts of catalyst taken were based on the SbW_9O_{33} content for a given amount of substrate. Yields were determined by GC analysis based on alcohol conversion and the product selectivity.

[a] After 8 h.

peroxo species formed was estimated to be six per unit of $[SbW_9O_{33}]$ by titrating the dichloroethane solution of the peroxo intermediate complexes with methanolic Ce(IV) [33].

Cyclohexanol oxidation experiments over $MTCA^+Cl^-$ yielded no oxidation products indicating that the phase transfer agent as such is not responsible for the oxidation reaction. The product yield was low (<10%) when the same reaction was carried out with $Na_9[SbW_9O_{33}]$ in the absence of any phase transfer catalysts even after 4 h at 80 °C (Table 2) indicating the need for a phase transfer catalyst to facilitate the reaction. In addition, an experiment was carried out the cyclohexanol oxidation reaction using $Na_9[SbW_9O_{33}] + MTCA^+Cl^-$ catalyst system under the open air without H_2O_2 which did not give any noticeable amount of cyclohexanone, indicating that dioxygen of air does not play any role in the above oxidation reaction under the present experimental condition.

3.3. Reusability and stability of the catalyst

Reusability experiments of the present catalytic system were carried out for oxidation of cyclohexanol as a probe reaction, in a similar manner as described for Na_2WO_4 based catalytic system [18]. After completion of the oxidation reaction, the organic product and the unreacted alcohols, if any, were distilled off carefully after washing several times with saturated aqueous $Na_2S_2O_3$. The distillation residues with fresh addition of $MTCA^+Cl^-$ were used for second and third runs where the yields were 91 and 92%, respectively.

The results from IR studies on the fresh, hydrogen peroxide treated and further KI treated samples clearly indicate that
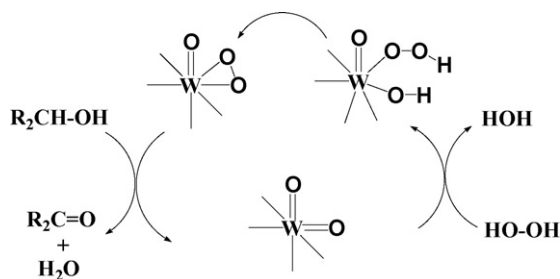
the $[SbW_9O_{33}]^{9-}$ part is stable in the presence of a phase transfer catalyst like $MTCA^+Cl^-$. However, in absence of a phase transfer catalyst, $Na_9[SbW_9O_{33}]$ formed a cloudy precipitate on interaction with aq. H_2O_2 which probably indicate that $Na_9[SbW_9O_{33}]$ decomposes in absence of a phase transfer catalyst. No such precipitation of the catalyst could be noticed when aq. H_2O_2 was added in the presence of a phase transfer catalyst and/or organic substrate like cyclohexanol. Similar experiments with Na_2WO_4 in the absence of a phase transfer catalyst resulted in immediate color change to yellow upon addition of aq. H_2O_2. Similarly, on addition of aq. H_2O_2 to a well established Zn ion substituted polyoxotungstate, $Na_{12}[WZn_3(ZnW_9O_{34})_2]$ [34], the solution turned yellow and also precipitate was noticed after leaving the solution for 3 days, probably indicating slow decomposition of $Na_{12}[WZn_3(ZnW_9O_{34})_2]$ compared to fast decomposition of $Na_9[SbW_9O_{33}]$ on reacting with aq. H_2O_2 in the absence of a phase transfer catalyst and/or organic substrate.

4. Conclusion

$Na_9[SbW_9O_{33}]$, in conjunction with a phase transfer catalyst (methyltricapryl ammonium chloride) is a highly efficient catalyst system for oxidation of alcohols using aq. H_2O_2. Most importantly the reactions can be carried out in the absence of any organic solvents especially halogenated solvents. The controlled experiments clearly indicate that the tungstate group is the active center for oxidation reaction. The formation of W-peroxo species was supported by IR measurement. Also, the catalyst was stable in the presence of a phase transfer catalyst with aq. H_2O_2 oxidant.

Acknowledgements

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Scheme 1. Proposed model for the reaction mechanism for oxidation of alcohols (only single tungsten octahedron is shown for clarity).

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