

# [SbW<sub>9</sub>O<sub>33</sub>]-based polyoxometalate combined with a phase transfer catalyst: A highly effective catalyst system for selective oxidation of alcohols with H<sub>2</sub>O<sub>2</sub>, and spectroscopic investigation

Rohit H. Ingle, N.K. Kala Raj, P. Manikandan \*

*Catalysis and Inorganic Chemistry Division, National Chemical Laboratory, Dr. Homibhabha Road, Pune 411 008, India*

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## Abstract

Na<sub>9</sub>[SbW<sub>9</sub>O<sub>33</sub>] in conjunction with a phase transfer catalyst, methyltricapryl ammonium chloride, is highly efficient for selective oxidation of variety of alcohols with aq. H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub>. 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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**Keywords:** Na<sub>9</sub>[SbW<sub>9</sub>O<sub>33</sub>]; Polyoxometalate; Polyoxotungstate; Phase transfer catalyst; Oxidation; Alcohol; Aq. H<sub>2</sub>O<sub>2</sub>

## 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<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> as oxidants [6–17]. For the usage of H<sub>2</sub>O<sub>2</sub> as an oxidant, transition metal ions based catalysts with d<sup>0</sup> 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<sub>2</sub>O<sub>2</sub> dismutation reaction [13–17]. Noyori and group used Na<sub>2</sub>WO<sub>4</sub> in conjunction with a special phase transfer catalyst bearing

HSO<sub>4</sub> 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<sub>2</sub>WO<sub>4</sub> 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<sub>2</sub>O<sub>2</sub>.

Here, we report Na<sub>9</sub>[SbW<sub>9</sub>O<sub>33</sub>] in conjunction with a commonly available phase transfer compound, methyltricapryl

\* Corresponding author. Tel.: +91 20 25902271; fax: +91 20 25902633.  
E-mail address: [p.manikandan@ncl.res.in](mailto:p.manikandan@ncl.res.in) (P. Manikandan).

ammonium chloride ( $\text{MTCA}^+\text{Cl}^-$ ), as a highly efficient catalyst system for selective oxidation of alcohols with aq.  $\text{H}_2\text{O}_2$  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  $\text{Sb}_2\text{O}_3$  were purchased from Loba Chemie, India. Aq.  $\text{H}_2\text{O}_2$  (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  $10 \text{ K min}^{-1}$  from 303 to 873 K under  $\text{N}_2$  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

$\text{Na}_9[\text{SbW}_9\text{O}_{33}]$  was prepared as per the reported literature [30,31] and their structures were confirmed by IR and elemental analysis.  $[\text{MTCA}]_9[\text{SbW}_9\text{O}_{33}]$  was prepared by exchanging the sodium ions of  $\text{Na}_9[\text{SbW}_9\text{O}_{33}]$  with  $\text{MTCA}^+\text{Cl}^-$  and then extracted into  $\text{C}_2\text{H}_4\text{Cl}_2$  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  $\text{Na}_x[\text{MTCA}]_{9-x}[\text{SbW}_9\text{O}_{33}]$  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  $\text{Na}_9[\text{SbW}_9\text{O}_{33}]$  and 0.09 mol of  $\text{MTCA}^+\text{Cl}^-$ , 10 mmol of alcohol and 15 mmol of 30% aq.  $\text{H}_2\text{O}_2$  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  $50 \text{ m} \times 0.32 \text{ mm}$  5% phenyl methylsilicone

capillary column and with  $\text{N}_2$  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

$\text{Na}_9[\text{SbW}_9\text{O}_{33}]$  in conjunction with a phase transfer compound,  $\text{MTCA}^+\text{Cl}^-$ , was used as a catalyst system for oxidation of variety of alcohols using aq.  $\text{H}_2\text{O}_2$  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.  $\text{H}_2\text{O}_2$  over  $\text{Na}_9[\text{SbW}_9\text{O}_{33}] + \text{MTCA}^+\text{Cl}^-$  catalyst system was carried out with cyclohexanol:aq.  $\text{H}_2\text{O}_2$  mol ratio of 1:1.5 in the temperature range  $40\text{--}80^\circ\text{C}$ . 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  $40^\circ\text{C}$  maximum the cyclohexanol conversion of  $\sim 74\%$  was obtained after 24 h whereas at 55 and  $60^\circ\text{C}$  the cyclohexanol conversions were about 83 and 84% after 8 and 5 h, respectively. However, at  $80^\circ\text{C}$  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  $60^\circ\text{C}$  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:  $17.74 \pm 0.14 \text{ kcal/mol}$ ,  $\Delta H_{298}^\ddagger$ :  $10.2 \pm 0.14 \text{ kcal/mol}$ ,  $\Delta S_{298}^\ddagger$ :  $10.2 \pm 0.14 \text{ kcal/mol}$ . The

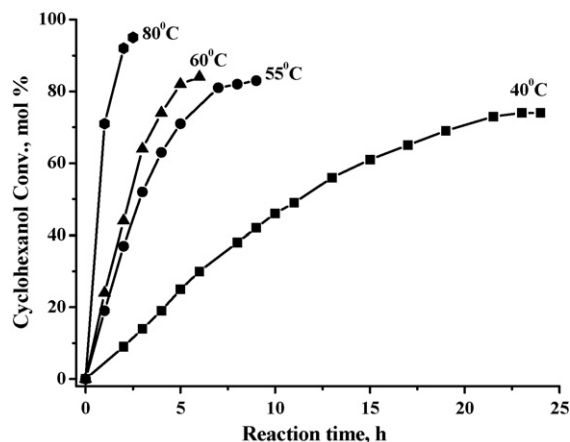


Fig. 1. Kinetic plots of oxidation of cyclohexanol over  $\text{Na}_9[\text{SbW}_9\text{O}_{33}] + 9 \text{ MTCA}^+\text{Cl}^-$  at different temperatures in the range  $40\text{--}80^\circ\text{C}$ . Cyclohexanone was the only product. Reaction condition—catalyst: 0.01 mmol, methyltricaprylammonium chloride: 0.09 mmol, alcohol: 10 mmol, 30% aq.  $\text{H}_2\text{O}_2$ : 15 mmol.

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