Catalytic Oxidation of Aromatic Hydrocarbons and Sulphides by Heteropoly Metalates

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Abstract
Oxidising behaviour of both simple and substituted heteropoly compounds was investigated under homogeneous conditions in the presence of \( \text{H}_2\text{O}_2 \) and \( \text{t-BuOOH} \) with organic sulphides and alkyl benzenes as substrates. Activity of these catalysts depends on the nature of the substrates used as well as the oxidising agent employed. The mechanistic aspects of the reaction are also elucidated.

Introduction
The traditional reagents employed in stoichiometric amounts for the conversion of methylbenzenes to the corresponding benzoic acids are potassium permanganate or chromyl compounds. Transition metals catalyzed reactions with aromatics give products derived from side chain oxidation as well as nuclear hydroxylation of aromatics. The important reaction is the oxidation of phenol to yield catechol and hydroquinone. Transition metal substituted silicalites (TS-1 and VS-2) [1,2] and vanadium-substituted heteropolymolybdates have also been used for the hydroxylation of phenol. The purpose of this communication is to study the oxidation of alkylaromatics using heteropolymolybdates with oxidizing agents like hydrogen peroxide and tert-butyl hydroperoxide (t-BuOOH) with a view to (i) to examine the differences in the product selectivities and (ii) to elucidate the mechanistic differences of the oxidation reaction with respect to the oxidizing agents.

Experimental
All the heteropoly compounds used in this study are formed by the condensation of the constituent oxides adopting the procedures given in literature [3,4].

(i) Oxidation of Sulphides
Oxidation of organic sulphides was carried out 303 K using \( \text{CH}_3\text{CN} \) as solvent. 0.103 m mol of the catalyst was used. Substrate to hydrogen peroxide ratio was take as 2 mol. Hydrogen peroxide was added dropwise with continuous stirring. Reaction time for methyl sulphide was 30 min, 180 and 225 mins for n-propyl and phenyl sulphides respectively. Products were extracted into dichlormethane. Phenyl sulphide and sulphone were separated using preparatory thin Layer chromatographic technique and \(^1\text{H}-\text{NMR} \) and melting point confirmed the products.

(ii) Oxidation of Alkyl benzenes
Oxidation of alkyl benzenes was carried out at 303 K for three hours with aceotonitrile as solvent. Hydrogen peroxide/substrate ratio of 2.5 mol was used in these experiments. Products extracted into dichloromethane and the catalyst was removed by washing with water.

(iii) Oxidation in the presence of t-BuOOH
0.103 mmol of the catalyst was dissolved in aceetonitrile, to this around 8-11 mmol of organic substrates and 9 mmol of \( \text{t-BuOOH} \) were added with continuous stirring. In all the cases the products were extracted into dichlormethane. Phenyl sulphide and sulphone were separated using preparatory thin Layer chromatographic technique and \(^1\text{H}-\text{NMR} \) and melting point confirmed the products. Quantitative determination was carried out by gas chromatography. \(^{31}\text{P} \) NMR spectra of the catalyst in \( \text{CH}_3\text{CN}-\text{H}_2\text{O} \) mixture at room temperature before and after adding hydrogen peroxide and also after reaction time were recorded using Jeol GSX 400 NB FT NMR. 85% \( \text{H}_3\text{PO}_4 \) was used as external standard and \( \text{D}_2\text{O} \) capsule
was used to record H decoupled spectra. IR spectrum of the reduced catalyst separated after two hours of the reaction time were recorded using KBr pellet.

**Results and discussion**

The results obtained for the catalytic oxidation of alkyl benzenes using \( \text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40} \) as typical catalysts are given in Tables 1 and 2 for hydrogen peroxide and t-BuOOH as oxidizing agents respectively. The main differences are:

(i) Ring hydroxylation is observed in presence of hydrogen peroxide while only side chain oxidation is observed with t-BuOOH as oxidizing agent.

(ii) The extent of percent conversion is higher when t-BuOOH is used as oxidizing agent. (iii) With hydrogen peroxide as oxidizing agent, the percent of higher oxygenated and unidentified products is higher.

The oxidation of two sulphides by both the oxidizing agents was studied on a number of heteropoly compounds as catalysts and the results obtained are given in Table 3. The points that emerge from the results given in this table are: (i) Increase in vanadium content increases sulphide conversion when t-BuOOH is used as oxidizing agent, while the opposite is observed with hydrogen peroxide as oxidizing agent. (ii) No sulphone is observed with t-BuOOH while sulphone is observed as one of the products when hydrogen peroxide is used as oxidizing agent.

**Table 1**

Catalytic Oxidation of alkyl benzenes using \( \text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40} \) hydrogen peroxide system at 303 K for 3 hrs

| Substrate       | Percent conversion | Percent product selectivity |
|-----------------|--------------------|----------------------------|
|                 |                    | Side chain oxidation | Ring hydroxylation | Others* |
| Toluene         | 25.6               | 7.7                  | 91.5              | <1      |
| Ethybenzene     | 25.8               | 85.9                 | 19.9              | 2.4     |
| O-Xylene        | 12.4               | 67.4                 | 19.9              | 12.7    |
| P-Xylene        | 23.2               | 75.3                 | 9.9               | 14.8    |
| Isopropybenzene | 26.2               | 47.9                 | 39.7              | 12.4    |
| Chlorobenzene   | 30.7               | -                    | 100.0             | -       |
| 124-trimethyl benzene | 9.1 | 81.2 | 11.6 | 7.2 |
| 135- trimethyl benzene | 11.3 | 94.2 | -    | 5.8 |

* higher oxygenated and unidentified products

**Table 2**

Catalytic oxidation of alkyl benzene using \( \text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40} \) – t-BuOOH system at 303 K for 3 hrs.

| Substrate       | Percent conversion | Percent selectivity |
|-----------------|--------------------|---------------------|
|                 |                    | Aldehyde or ketone | alcohol | others |
| Toluene         | 30.3               | 79.9                | 19.8     | <1     |
| Ethyl benzene   | 42.2               | 60.4                | 35.6     | 4.0    |
| O-Xylene        | 14.1               | 83.9                | 14.5     | 1.6    |
| p-Xylene        | 26.2               | 72.2                | 19.1     | 8.7    |
| Isopropybenzene | 35.7               | 64.1                | 26.8     | 9.1    |
Table 3
Oxidation of sulphides on heteropoly compounds with hydrogen peroxide and tert-butylhydroperoxide at 303 K.

| Catalyst                  | Methyl sulphide | Phenyl sulphide |
|---------------------------|-----------------|-----------------|
|                           | $\text{H}_2\text{O}_2$ (30 min) | $\text{t-BuOOH}$ (30 min) | $\text{H}_2\text{O}_2$ (225 min) | $\text{t-BuOOH}$ (225 min) |
| $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ | 69.2            | 38.3            | 87.9(75.6)     | 62.5          |
| $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ | 67.2            | 48.6            | 83.1(14.8)     | 69.2          |
| $\text{H}_3\text{PV}_{2}\text{Mo}_{10}\text{O}_{40}$ | 51.8            | 50.1            | 80.9(74.4)     | 72.3          |
| $\text{H}_4\text{PV}_{1}\text{Mo}_{6}\text{O}_{40}$ | 44.4            | 55.1            | 78.1(71.9)     | 76.4          |
| $\text{H}_4\text{PV}_{2}\text{W}_{10}\text{O}_{40}$ | 55.9            | 44.9            | 82.4(73.1)     | 65.2          |
| $\text{H}_4\text{PMo}_{6}\text{W}_{6}\text{O}_{40}$ | 61.9            | 36.9            | 86.2(75.1)     | 59.3          |
| $\text{K}_7\text{Pt}_{2}\text{W}_{10}\text{O}_{40}$ | 42.2            | 33.9            | 71.9(74.3)     | 41.1          |

The catalytic decomposition of hydrogen peroxide is more vigorous than the decomposition of $\text{t-BuOOH}$ as the binding constant of hydrogen peroxide to the metal ions is about $10^7$ times greater than that of alkyl hydroperoxide [5]. Though similar peroxy species may be formed as the reaction intermediate on interaction of the oxidizing agent with the metal ions, the reactivity of these peroxy species appears to be different. Detailed spectroscopic investigation of the heteropoly compounds after interaction with both the oxidizing agents was carried out for this purpose. $^{31}\text{P}$ NMR spectra of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ in CH$_3$CN-water mixture before and after adding hydrogen peroxide and also after 1 or 2 hours of reaction time at 333K in the absence of hydrogen peroxide are shown in Figs. 1 and 2. A single sharp peak at $-3.2$ ppm was observed for 12-molybdophosphoric acid [6,7]. On addition of hydrogen peroxide this peak completely disappeared and a new peak at 4.1 ppm was observed. This shows complete change in Keggin structure on addition of hydrogen peroxide. It is known that molybdophosphoric acid forms peroxy species like heteropoly tungstate [8]. Molybdenum peroxy species gives a $^{31}\text{P}$ NMR signal around 7 ppm [9]. To confirm this molybdenum peroxy species was formed by adding excess hydrogen peroxide to heteropolytungstic acid and separating it by the addition of cetyl trimethyl ammonium chloride [10]. The $^{31}\text{P}$ NMR spectrum of this species in dichloromethane gave a signal at 5.6 ppm. In the absence of hydrogen peroxide the reaction proceeded by electron transfer to give a reduced catalyst. As the anionic charge increases $^{31}\text{P}$ environment becomes more shielded and

Fig. 1. $^{31}\text{P}$-nmr spectra of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ in CH$_3$CN-H$_2$O mixture (a) before (b) after addition of H$_2$O$_2$ at RT.
this is reflected by many $^{31}\text{P}$ NMR signals in the upfield region between $-4$ and $-12.9$ ppm. The assignments of these peaks are given in Table 4. The results presented in Table 4 reflect that the structure of the catalyst does not collapse in the absence of hydrogen peroxide.

| Chemical species (number of added electrons) | $^{31}\text{P}$ chemical shift (ppm) |
|---------------------------------------------|-------------------------------------|
| $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ | $-3.2$ or $-3.9$ |
| $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40}$ (IV) | $-4.1$ or $-4.6$ |
| $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40}$ (II) | $-5.16$ or $-5.8$ |
| $\beta\text{-H}_3\text{PMo}_{12}\text{O}_{40}$ (II) | $-5.49$ or $-6.0$ |
| $\beta\text{-H}_3\text{PMo}_{12}\text{O}_{40}$ (IV) | $-12.9$ or $-12.9$ |

$^{31}\text{P}$ NMR spectra of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ in CH$_3$CN-water mixture after adding t-BuOOH and after one hour reaction time at 335 K are shown in Fig. 3. The spectrum shows a single peak in presence of t-BuOOH at 4.1 ppm and after one hour reaction no change in the spectrum of the catalyst was observed. No peaks in the upfield region were observed like that of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ – hydrogen peroxide system. This indicates that the structure of the Keggin unit did not change even after adding t-BuOOH.

The IR spectrum of the reduced catalyst after two hour reaction time without oxidizing agent showed no dramatic changes revealing minor shift and splitting.
of some bands and a retention of the structure as a whole. However deep reduction of the catalyst with further introduction of electrons into the Keggin anion drastically changes the IR spectrum of the heteropoly- molybdate, namely high background is superimposed into the vibrational bands of the anion and the intensities of the P-O and M-O-M stretching vibrations are markedly decreased [11]. P-O asymmetric stretching vibration, which was observed around 1064 cm⁻¹, in the original catalyst, shows two bands at 1116.8 and 1065.6 cm⁻¹ in the reduced catalyst. ³¹P NMR spectrum of vanadomolybdophosphoric acid in the presence and absence of hydrogen peroxide are shown in Fig.4. Peaks are observed around –3.7 to-4.4 ppm which are characteristic of vanadium substitution [13]. Unlike molybdophosphoric acid, vanadium substituted heteropoly- molydates do not show any shift in the peak after adding hydrogen peroxide. This indicates that H₅PV₂Mo₁₀O₄₀ does not undergo structural collapse in the presence of hydrogen peroxide. There was only enhancement in the intensity of the peaks due to the interaction of hydrogen peroxide with the vanadium centre . Neuman et al [14] have shown that vanadium substituted heteropoly- molybdate gives the peroxospecies as an intermediate whereas H₃PMO₁₂O₄₀ gives isolable peroxospecies as an intermediate, which has a different structure from the Keggin structure. ³¹P NMR spectra of H₃PMO₁₂O₄₀ in CH₃CN- water mixture after adding t-BuOOH and after one hour of reaction at 335K are shown in Fig.3. H₃PMO₁₂O₄₀ was taken as an example to study the formation of peroxospecies in presence of t-BuOOH mainly because this catalyst showed drastic changes in the presence of hydrogen peroxide. ³¹P NMR spectrum of H₃PMO₁₂O₄₀ in presence of t-BuOOH shows a single sharp peak around 4.1 ppm and after one hour of reaction no change in the spectrum of the catalyst was observed. No peaks in the upfield region were observed like that of H₃PMO₁₂O₄₀- hydrogen peroxide system. This indicates that the structure of the Keggin unit did not change even after adding t-BuOOH. IR spectrum of the catalyst remains unaltered after adding t-buOOH. Similar behavior was reported by Schwegler et al [15]. These results show that H₃PMO₁₂O₄₀–t-BuOOH system donot produce any isolable peroxo- species like that of H₃PMO₁₂O₄₀–H₂O₂ system but may form them as reaction intermediate as proposed for vanadium substituted heteropoly compounds.

![Fig.4. ³¹P-nmr spectra of H₅PV₂Mo₁₀O₄₀ in CH₃CN-H₂O mixture (a) before (b) after addition of H₂O₂ at room temperature.](image)

Reaction mechanism proposed by Mimoun et al [16] for the oxidation of alkyl benzene is shown in Scheme 1.

Hydrogen peroxide interacts with the vanadium centre to form vanadium peroxy species, which transfers oxygen to the hydrocarbon in a bimolecular fashion, and the hydroxylation of the aromatic hydrocarbon takes place by the homolytic addition of the electrophilic radical species to the aromatic ring. Vanadium peroxy complexes which homolytically cleave to give electrophilic reactive species behave differently from known complexes of molybdenum which are effec-
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Scheme 1.

Scheme 2.

Scheme 3.

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