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Catalytic Oxidation of Aromatic Hydrocarbons and Sulphides by Heteropoly Metalates

B.Viswanathan and Athilakshmi

Department of Chemistry

Indian Institute of Technology, Madras 600 036, India.

Abstract

Oxidising behaviour of both simple and substituted heteropoly compounds was investigated under homogeneous conditions in the presence of H_2O_2 and 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 CH_3CN 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}H-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 dichlormethane 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 acetonitrile, to this around 8-11 mmol of organic substrates and 9 mmol of 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}H-NMR and melting point confirmed the products. Quantitative determination was carried out by gas chromatography.

^{31}P NMR spectra of the catalyst in CH_3CN-H_2O 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% H_3PO_4 was used as external standard and D_2O capsule

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*corresponding author. E-mail: bviswanathan@hotmail.com

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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 $H_5PV_2Mo_{10}O_{40}$ 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 $H_5PV_2Mo_{10}O_{40}$ 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
Isopropylbenzene	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 alkylbenzene using $H_5PV_2Mo_{10}O_{40}$ – 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
Isopropylbenzene	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	
	H_2O_2 (30 min)	t-Bu OOH (30 min)	H_2O_2 (225 min)	t-BuOOH (225 min)
$H_3PMo_{12}O_{40}$	69.2	38.3	87.9(75.6)	62.5
$H_4PVMo_{11}O_{40}$	67.2	48.6	83.1(14.8)	69.2
$H_5PV_2Mo_{10}O_{40}$	51.8	50.1	80.9(74.4)	72.3
$H_6PV_3Mo_9O_{40}$	44.4	55.1	78.1(71.9)	76.4
$H_5PV_2W_{10}O_{40}$	55.9	44.9	82.4(73.1)	65.2
$H_3PMo_6W_6O_{40}$	61.9	36.9	86.2(75.1)	59.3
$K_7Pti_2W_{10}O_{40}$	42.2	33.9	71.9(74.3)	41.1

The catalytic decomposition of hydrogen peroxide is more vigorous than the decomposition of t-BuOOH as the binding constant of hydrogen peroxide to the metal ions is about 10^3 times greater than that of alkyl hydroperoxide [5].

Though similar peroxo species may be formed as the reaction intermediate on interaction of the oxidizing agent with the metal ions, the reactivity of these peroxo 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}P NMR spectra of $H_3PMo_{12}O_{40}$ in CH_3CN-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]. Om additionof hydrogen peroide 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 peroxo species like heteropoly tungstate [8]. Molybdenum peroxo species gives a ^{31}P NMR signal around 7 ppm [9]. To confirm this molybdenum peroxo species was formed by adding excess hydrogen peroxide to heteropolymolybdic acid and separating it by the addition of cetyl trimethyl ammonium chloride [10]. The ^{31}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}P environment becomes more shielded and

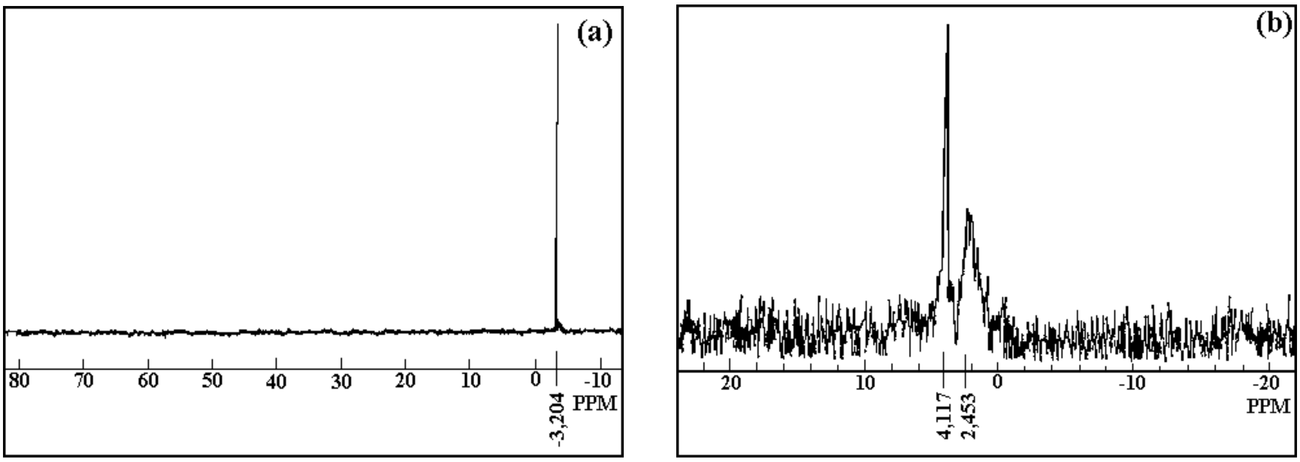


Fig.1. ^{31}P-nmr spectra of $H_3PMo_{12}O_{40}$ in CH_3CN-H_2O mixture (a) before (b) after addition of H_2O_2 at RT.

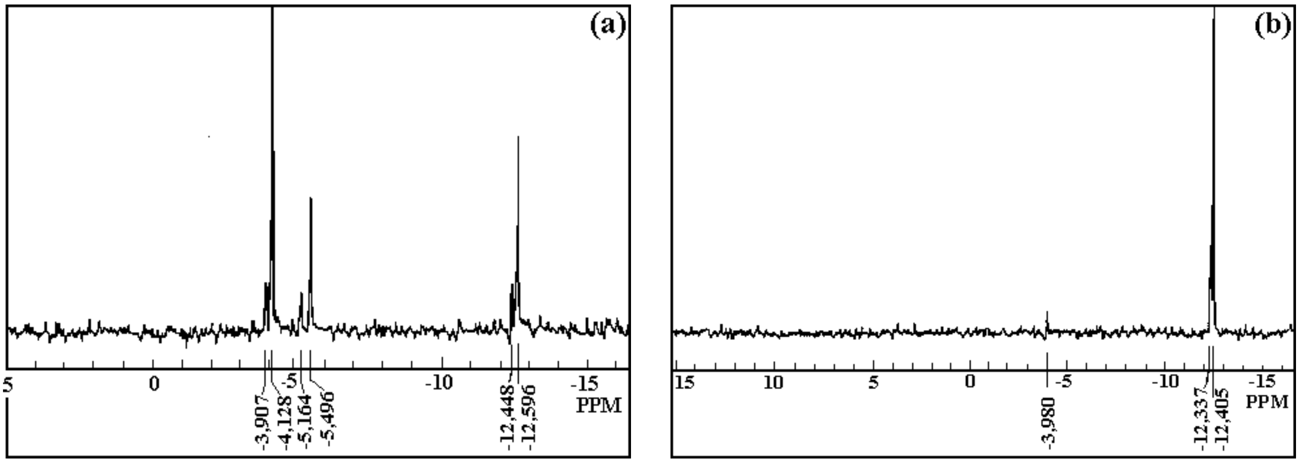


Fig.2. ^{31}P-nmr spectra of $H_3PMo_{12}O_{40}$ in CH_3CN-H_2O mixture (a) after one hr reaction time (b) two hrs reaction time at 333 K.

this is reflected by many ^{31}P NMR signals in the up field 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.

Table 4

Correlation between ^{31}P chemical shift and different reduced species of $H_3PMo_{12}O_{40}$

Chemical species (number of added electrons)	^{31}P chemical shift (ppm)
$H_3PMo_{12}O_{40}$	-3.2 or -3.9
α-$H_3PMo_{12}O_{40}$ (IV)	-4.1(-4.6)
α-$H_3PMo_{12}O_{40}$ (II)	-5.16(-5.8)
β-$H_3PMo_{12}O_{40}$ (II)	-5.49(-6.0)
β-$H_3PMo_{12}O_{40}$ (IV)	-12.9(-12.9)

^{31}P NMR spectra of $H_3PMo_{12}O_{40}$ in CH_3CN-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 $H_3PMo_{12}O_{40}$ – 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

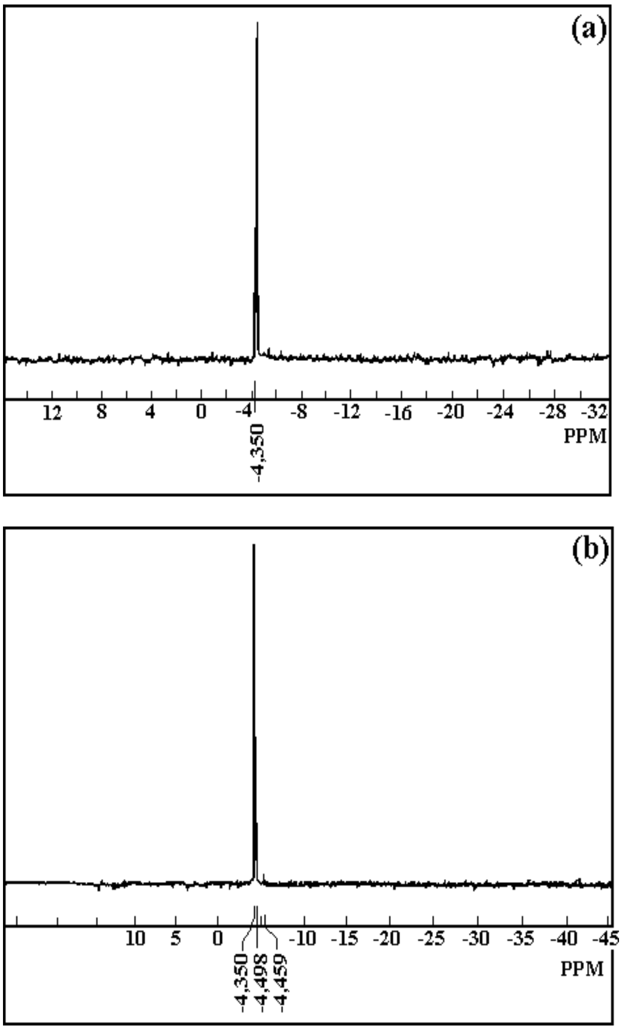


Fig.3. ^{31}P-nmr spectra of $H_3PMo_{12}O_{40}$ in CH_3CN-H_2O mixture (a) after adding t-BuOOH (b) after one hr reaction time at 335 K.

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. ^{31}P NMR spectrum of vanadomolybdophos- phoric 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 heteropolymolydates do not show any shift in the peak after adding hydrogen peroxide. This indicates that $H_5PV_2Mo_{10}O_{40}$ 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 heteropolymolybdate gives the peroxospecies as an intermediate whereas $H_3PMo_{12}O_{40}$ gives isolable peroxospecies as an intermediate, which has a different structure from the Keggin structure. ^{31}P NMR spectra of $H_3PMo_{12}O_{40}$ in CH_3CN- water mixture after adding t-BuOOH and after one hour of reaction at 335K are shown in Fig.3. $H_3PMo_{12}O_{40}$ 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. ^{31}P NMR spectrum of $H_3PMo_{12}O_{40}$ 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 $H_3PMo_{12}O_{40}$ – 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 $H_3PMo_{12}O_{40}$ –t-BuOOH system donot produce any isolable peroxo- species like that of $H_3PMo_{12}O_{40}$ – H_2O_2 system but may form them as reaction intermediate as proposed for vanadium substituted heteropoly compounds.

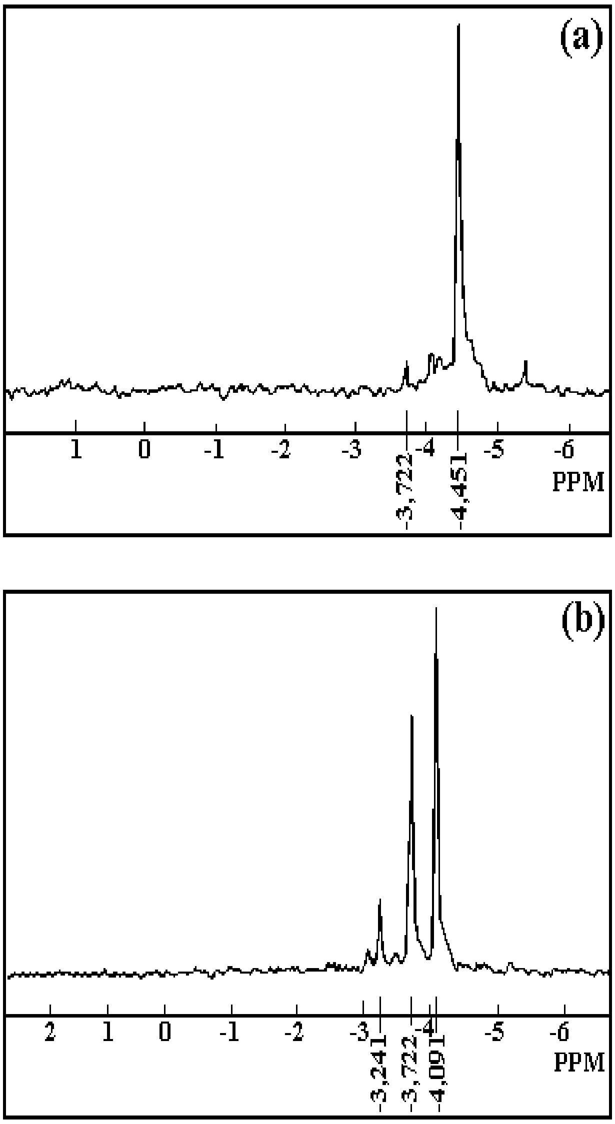
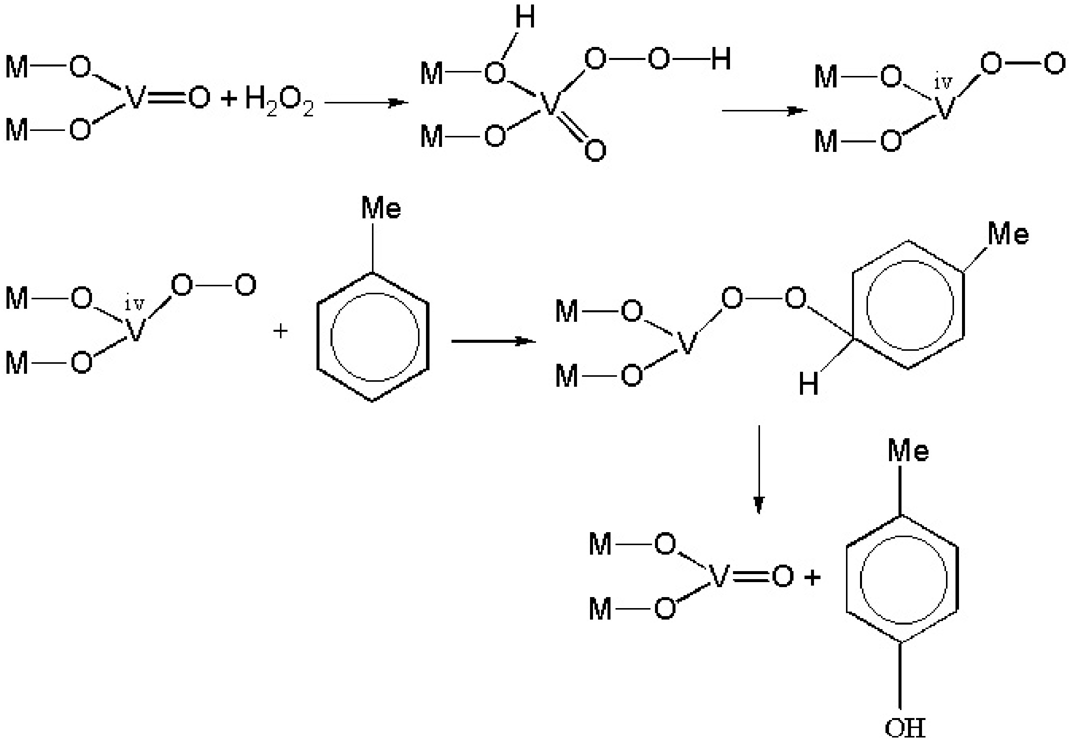


Fig.4. ^{31}P-nmr spectra of $H_5PV_2Mo_{10}O_{40}$ in CH_3CN-H_2O mixture (a) before (b) after addition of H_2O_2 at room temperature.

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 peroxo 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 peroxo complexes which homolytically cleave to give electrophilic reactive species behave differently from known complexes of molybdenum which are effec-

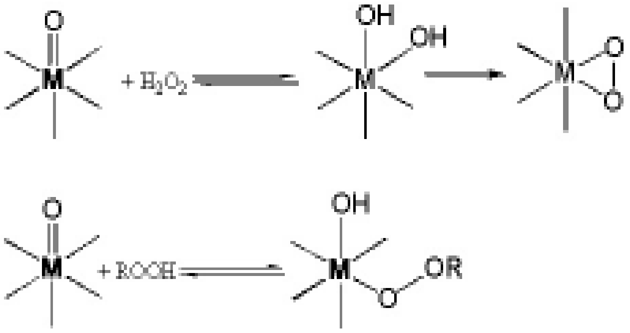
Scheme 1.



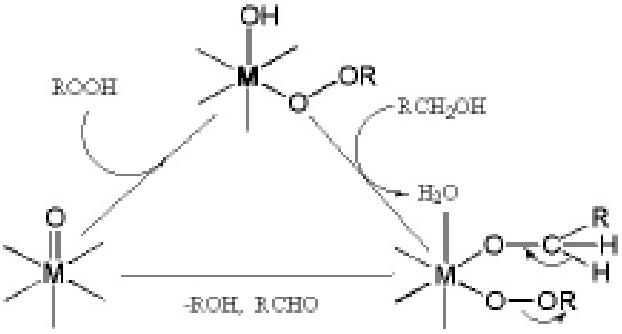
tive for epoxidation of olefins but not as hydroxylating agents. This may be the reason for the ineffectiveness of the $H_3PMo_{12}O_{40}/H_2O_2$ system for these reactions. This type of mechanism was also suggested by Huybrechts et al [17]. In the case of alkylhydroperoxide the open type of peroxo species has been proposed (Scheme 2).

This will account for the difference in reactivity for the oxidation of different substrates in presence of t-BuOOH and hydrogen peroxide. The general mechanism for the oxidation of alcohol in presence of t-BuOOH can be given in Scheme 3.

Scheme 2.



Scheme 3.



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