Catalytic Studies Involving Heteropoly Acids and Related Compounds

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This Thesis is Dedicated
to my beloved parents

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CHAPTER –1

INTRODUCTION

1.0 Introduction

Catalysis by heteropolyacids (HPA) and related compounds is a field of growing importance, attracting attention worldwide in which many novel and exciting developments are taking place, both in the areas of research and technology. Heteropolyacids belong to the family of polyoxometalates that incorporates anions (heteropolyanions) having metal-oxygen as the basic structural unit. The octahedra are linked together and form an extremely stable and compact skeleton of the heteropolyanions. The cations may be hydrogen, alkali metal and other metal ions. More than twenty types of structures, incorporating four to forty metal atoms and from one to nine heteroatoms are known for molybdenum, tungsten, vanadium and niobium heteropolyanions [1]. Some of the commonly known series of heteropolyanions are shown in Table-1

Table-1

Common Heteropolyacids

X/M	Structure	Formula	Negative charge	X^{n+}
1/12	Keggin (typeA) Silverton (typeB)	$XM_{12}O_{40}$ $XM_{12}O_{42}$	8-n 8	P^{5+},As^{5+},Si^{4+}, Ge^{4+},C^{4+} Ce^{4+}, Th^{4+}
1/11	Keggin-like (lacunary)	$XM_{11}O_{39}$	12-n	P^{5+},As^{5+}, Ge^{4+}
2/18	Dawson	$X_2M_{18}O_{62}$	6	P^{5+},As^{5}
1/9	Waugh	XM_9O_{32}	6	Mn^{4+}, Ni^{4+}
1/6	Anderson (typeA) Anderson (typeB)	XM_6O_{24} XM_6O_{24}	12-n 6-n	Te^{6+}, I^{7+} Co^{3+}, Al^{3+}, Cr^{3+}

M = W^{6+}, Mo^{6+}, etc.

The commonest compounds belonging to the saturated 12th series (M:X = 12) are of the greatest importance in catalysis. These Keggin type heteropolyacids are the most stable, more easily available and have been studied in more detail. They contain the heterododecametalates with the formula $XM_{12}O_{40}^{x-8}$ having the Keggin structure where X is the central or the heteroatom (Si^{4+}, Ge^{4+}, P^{5+}, As^{5+} etc), x the degree of its oxidation state and M is the metal atom (Mo^{6+}, W^{6+}) which can be partly replaced by other metals.

Well-defined Keggin structure is composed of a central XO_4 tetrahedron surrounded by twelve edge and corner sharing metal-oxygen octahedra (MO_6) units. These compounds are nearly always negatively charged although the negative charge density is widely variable depending on the elemental composition and molecular structure. Heterpolyanions are polymeric oxoanions formed by the condensation of more than two different mononuclear oxoanions in acidic medium as shown in the equation

$pX^{x+}O_r + qM^{m+}O_n + zH^+ \rightarrow X_pM_qO_s^{(p.x+m.q-z.s)} + z/2\ H_2O$

with M = metal

X = hetero-atom

x = valency of hetero-atom

m = valency of the addenda atom

and s+z/2 = n.q + r.p (oxygen balance)

for example

$PO_4^{3-} + 12MoO_4^{2-} + 24H^+ \rightarrow PMo_{12}O_{40}^{3-} + 12H_2O$

Although the elements that can function as addenda atoms, M, in heteropoly or isopolyanions, appear to be limited to those with both a favourable combination of ionic radius, charge and the ability to form $d\pi$-$p\pi$ M-O bonds and there is no such restriction on the heteroatom X. This thesis incorporates the work done on Keggin type heteropolyoxometalates. They are the most studied among all the structural types in the class of heteropoly compounds because of their stability and ease of synthesis.

1.1 History of Keggin heteropolyoxometalates.

It was in 1826 Berzelius described the yellow precipitate that is produced when ammonium molybdate is added to phosphoric acid and which is now known as ammonium12- molybdophosphate $(NH_4)_3(PMo_{12}O_{40})$ aq . However it was not until the discovery of tungstosilicic acids and their salts by Marginac in 1862 that the analytical composition of such heteropolyacids were precisely determined. But he did not propose a structure for the above compound which was later correctly analyzed as $SiO_2.12WO_3.2H_2O$. The first attempts to understand the composition of heteropolyanions were based on Werner's coordination theory. Structure determination for heteropoly compounds was not possible until the arrival of X-ray diffraction techniques. A hypothesis advanced by Miolati and Pizzighelli in 1908 was adopted and developed by Rosenheim. During the subsequent 25-30 years Rosenheim was probably the most productive and influential worker in the field of polyanion chemistry. According to the Miolati- Rosenheim (MR) theory heteropoly acids were based on six coordinate hetero atoms with MO_4^{2-} or $M_2O_7^{\ 2-}$ anions as ligands or bridging groups. Subsequent isolation of salts such as Cs_8 $[Si(W_2O_7)_6]$ and $(CN_3H_6)_7[P(W_2O_7)_6].12H_2O$ lent an early support to MR theory. The first serious criticism of the theory came from Pauling in 1929. While accepting the Rosenheim structure for 6:1complex, Pauling noted that molybdenum(VI) and tungsten(VI) had crystal radii appropriate for octahedral coordination by oxygen and proposed a structure for the 12:1 complex based on an arrangement of twelve molybdenum(VI) or tungsten(VI) octahedra surrounding a central XO_4 tetrahedra. The resulting formula were written as $H_4[SiO_4W_{12}(OH)_{36}]$, and these predicted the correct (observed) basicities. The structure was ultimately shown to be wrong in detail, since Pauling considered only the corner sharing between the MO_6 octahedra. After four years Keggin solved the structure of $H_3[PW_{12}0_{40}]$. $5H_2O$ by X-ray diffraction and showed that the anion was indeed based on WO_6 octahedra units as suggested, but these octahedra were linked by shared edges as well corners. Anions were confirmed shortly afterwards by Bradley and Illingworth's investigation of $H_3[PW_{12}0_{40}]$.$29H_2O$. Structure determination was based on powder photographs [1].

1.2 Nomenclature in Heteropolyoxometalates

The literature data on the nomenclature of heteropolycompounds have been. inconsistent. Older designation consisted of prefixing the names of the central atoms to the words "molybdate (tungstate)"or "molybdic (tungstic)"acid – for example, "phosphomolybdate" or " silicomolybdate". Greek prefixes were used to describe the number of atoms of the central element and molybdenum or tungsten i.e., dodecatungstosilicic acid. However the International Union of Pure and Applied Chemistry (IUPAC) uses a different system of nomenclature. Names of heteropolyanions begin with an Arabic numeral designating the simplest ratio of molybdenum or tungsten atoms to the central atom. This is followed by the prefix "molybdo" or "tungsto" and then by the name of the simple anion (or acid) which contains the central atom in the corresponding oxidation state. In case of ambiguity, Roman numerals may be used to designate the oxidation state of the central atom. Current knowledge of the structure and properties of heteropoly compounds necessitates a more adequate nomenclature of such compounds by taking into consideration both the structure and degree of polymerization and oxidation of the central atom. Proposed system of nomenclature is designed to extend the current IUPAC names to describe heteropoly compounds more adequately in cases where information about structure is currently available. In this system, the oxidation state of the central atoms as shown by a Roman numeral in parentheses. The prefix molybdo, tungsto or vanado designates the peripheral atoms, whereas the italicized prefix oct, tet, etc., indicates the stereochemistry (octahedral and tetrahedral) about the peripheral and the central atoms. Arabic numerals designate the ratio of the number of peripheral and the central atoms. The term dimeric, for example, preceding the name indicates the degree of polymerization of the heteropolyanion when known. A superscript Arabic numeral at the end of the name indicates the charge of the anion. The Greek letter designates bridging between central atoms [1]. Examples of nomenclature of the IUPAC and the proposed system are given in Table-2

Table-2

IUPAC Nomenclature in HPA

Formula	**Tentative IUPAC Names**	Proposed Names
$Na_3[P^{+5}Mo_{12}O_{40}]$	Trisodium dodecamolybdophosphate(V)	Sodium12-oct- molybdo-tet- phosphate(V)$^{3)}$
$H_4[SiW_{12}O_{40}]$	12- Wolframosilicic acid	12-Oct-tungsto-tet-silicic(IV)$^{4)}$ acid
$K_3[P^{+5}W_{12}O_{40}]$	**Tripotassium dodecatungstophosphate (V)**	Potassium12-oct-tungsto-tet- phosphate(V)$^{3)}$

1.3 Classification of heteropoly compounds

Heteropoly compounds may be classified according to the ratio of the number of central atoms to the peripheral molybdenum or other such atoms. Compounds with the same number of atoms in the anion usually are isomorphous and have similar chemical properties. Usually, the heteropolymolybdates and heteropolytungstates containing non-transition elements as central atoms have more structural analogues than those containing transition elements as central atoms [1].

Below in table-3 are the list of the elements known to be capable of acting as central atoms in heteropolycompounds.

Table-3

Central Atoms in Heteropoly compounds

Periodic Group	Element
I	H, Cu^{+2}
II	Be^{+2}, Zn^{+2}
III	B^{+3}, Al^{+3}, Ga^{+3}
IV	Si^{+4}, Ge^{+4}, Sn^{+4}(?), Ti^{+4}, Zr^{+4}, Th^{+4}, Hf^{+4}, Ce^{+3}, Ce^{+4}, and other rare earths
V	N^{+5}(?), P^{+3}, P^{+5}, As^{+5}, V^{+4}(?), V^{+5}, Sb^{+3}(?), Sb^{+5}(?), Bi^{+3}
VI	Cr^{+3}, S^{+4}, Te^{+4}, Te^{+6}
VII	Mn^{+2}, Mn^{+4}, I^{+7}
VIII	Fe^{+3}, Co^{+2}, Co^{+3}, Ni^{+2}, Ni^{+4}, Rh^{+3}, Pt^{+4}(?)

(?) = Doubtful existence of a heteropolyanion

1.4 Structure of Keggin heteropoly compounds

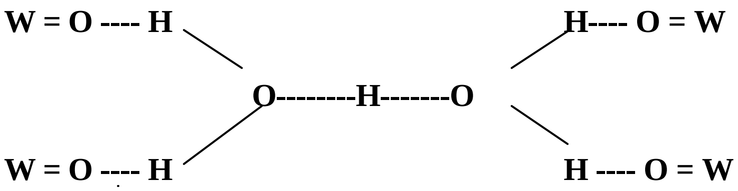
The Keggin type of heteropoly compound is an assembly of three kinds of structures. It is very important to distinguish between the primary, secondary and tertiary structure which are the building blocks of the complex [2].

1.4.1 Primary Structure

The heteropoly acids in the solid state are ionic crystals (sometimes amorphous) which consist of large polyanions that are linked together. This polyanionic Keggin structure specially the α type has T_d symmetry and consists of a centrally located XO_4 tetrahedron (X = heteroatom or central atom) surrounded by twelve edge and corner sharing MO_6 octahedra (M = addenda atom). The octahedra are arranged in four M_3O_{13} groups. Each group is formed by three octahedra sharing edges and having a common oxygen atom which is also shared with the central tetrahedron XO_4.The oxygen atoms in the Keggin structure are classified into four classes of symmetry equivalent oxygens:$X\text{-}O_a\text{-}M$, $M\text{-}O_b\text{-}M$ (“inter” bridges between corner sharing octahedra), $M\text{-}O_c\text{-}M$ (“intra bridges between edge sharing, i.e., within a M_3O_{13} set) and $M\text{-}O_d$ (the terminal oxygens) where M is the addenda atom and X is the heteroatom. The anion contains twelve quasilinear M-O-M linkages between the octahedra forming part of different M_3O_{13} triads twelve angular M O M bonds between the octahedra within a single triad, four X-O-M bonds where the triads are joined to the central atom, and twelve terminal M = O bonds.

1.4.2 Secondary Structure

The three dimensional arrangement consisting of the large polyanions, cations, water of crystallization, and other molecules constitute the secondary structure of heteropoly compounds. Acid forms of heteropoly compounds in solid state, contain counter cations or the protons which play an important role in the structre of the crystal, by linking the neighbouring heteropolyanions. For e.g., protons of crystalline $H_3PW_{12}O_{40}.6H_2O$ are presented in hydrated species, $H_5O_2^+$, each of which links four neighbouring heteropolyanions by hydrogen bonding to the terminal $W\text{-}O_d$ oxygen atoms, and the polyanions are packed in a bcc structure. This is shown in the figure



Secondary structures may also contain organic molecules for eg., $H_4SiW_{12}O_{40}.9DMSO$ which contains nine molecules of DMSO in a unit cell where there are weak hydrogen bonds between methyl groups and oxygen atom of the heteropolyanions. Another interesting example is $PW_{12}O_{40}.\ [(C_5H_5N)_2H]_3$ which is obtained by the reaction of anhydrous $H_3PW_{12}O_{40}$ with pyridine.

1.4.3 Tertiary Structure

Structure of the solid heteropolyacid as assembled constitutes the tertiary component of the complex. The size of the particles, pore structure and distribution of protons in particles are the elements of the tertiary structure.

1.5 General properties of Keggin Heteropoly compounds

The physical and chemical properties of heteropoly compounds are listed below [1]

1**. Heteropolycompounds generally have very high molecular weights ranging.over 2000.**

2. **Free acids and most salts of heteropolyanions are extraordinarily soluble in water and are often very soluble in a wide range of organic solvents.**

In water**: Most free acids are generally extremely soluble (up to 85 % by weight of solution). In general, the heteropoly salts of small cations, including those of many heavy metals, are also very soluble. Heteropoly with large size counter cations are less soluble.Thus Cs^+, Ag^+, Tl^+, Hg^{++}, Pb^{++} and the larger alkaline earth metal salts are often insoluble. The NH_4^+, K^+, and Rb^+ salts of some of the important series of heteropolyanions are insoluble. Salts of heteropolymolybdate.and heteropolytungstate anions with cationic coordination complexes, alkaloids, or organic amines are usually insoluble. Solubility of the heteropoly compounds in water must be attributed to very low lattice energies and solvation of cations. Solubility is governed by packing considerations.in the crystals. The counter cations are fitted in between the large negative anions. When large cations like Rb^+, Cs^+ are present they allow stable packing in the large interstices, causing sufficient lowering of lattice energy to produce insolubilty.**

In organic solvents**: Many of the free acids and a few of the salts are very soluble in organic solvents, especially if the latter contain oxygen. Ethers, alcohols, and ketones (in that order) are generally the best solvents. Free acids are insoluble in non-oxygensolvents such as benzene, chloroform and carbon disulphide. The**

dehydrated salts sometimes dissolve readily in organic solvents; the hydrated salts are insoluble.

3. **The crystalline free acids and salts of heteropolymolybdate and heteropolytungstate anions are almost always highly hydrated. A given acid or salt will often form several solid hydrates. Most of the heteropolymolybdate series form isomorphous 30-hydrates.They melt in their own water of hydration between 40 to 100°C. In dry air they begin to lose water and they give up all thirty water molecules in vacuum over sulphuric acid.**
4. **Many heteropoly compounds are highly coloured and the colours ranging through the spectrum and occuring in many shades. Heterpolymolybdates are generally yellow in solution and in crystal form. Partial substitution of the molybdenum atom/s by vanadium changes the colour from yellow to orange. The corresponding tungstates are pale yellow or colourless.**
5. **Some heteropoly compounds especially heteropolymolybdates are strong oxidizing agents and can be very readily changed to fairly stable, reduced heteropolymolybdates. These reduced species are called "heteropoly blues".**
6. **Heteropolytungstates and molybdates are strong acids. The acidity is generally determined by dissocation constants and the Hammet acidity function. The free acids generally have several replaceable hydrogen ions. Protons are dissociated completely from the structure in aqueous solution. Since in heteropolyacids the negative charge of similar value is spread over much larger anions than those from mineral acid and the electrostatic interactions between proton and the anion is much less for heteropolyacids than for mineral acids. An additional important**

factor is possibly the dynamic delocalizability of the charge or electron. The change in the electronic charge caused by deprotonation may be spread over he entire polyanion unit..

Acidity in solid HPA

The strength and the number of acid centers as well as related properties of heteropolyacids can be controlled by the structure and composition of heteropolyanions, the extent of hydration, the type of support, the thermal treatment, etc. Solid heteropolyacids such as $H_3PW_{12}O_{40}.xH_2O$ and $H_3PMo_{12}O_{40}.xH_2O$ are pure Bronsted acids and are stronger than conventional solid acids such as SiO_2-Al_2O_3 . Thermal desorption of basic molecules also reveals the acidic properties. Pyridine adsorbed on SiO_2 - Al_2O_3 is completely desorbed at 573 K. On the other hand, sorbed pyridine in $H_3PW_{12}O_{40}$ mostly remains at 573 K, indicating that $H_3PW_{12}O_{40}$ is a very strong acid. The acid strength can also be demonstrated by temperature- programmed desorption (TPD) of NH_3. The general trend for acid strength among the common heteropolyacids is as follows

$H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} \geq H_3PMo_{12}O_{40} > H_4SiMo_{12}O_{40}$

7. All heteropolymolybdates and heteropolytungstates are decomposed in strongly.basic solutions. The final degradation products of these compounds are simple molybdate or tungstate ions. Heteropolytungstates are more stable in acid solutions than the corresponding molybdates. Heteropolytungstates are hydrolytically more stable than the heteropoly molybdates. If a base is progressively added to a solution containing heteropolyanions, the pH of the solution gradually rises. The anion retains its identity through a certain range of pH until the pH of degradation of that particular anion is reached. After this stage the pH changes a little more as more base is added until the heteropolyanion is converted to a species stable at a higher pH range or is completely degraded to simple ions. Throughout specific ranges of pH and other conditions, most solutions of heteropolymolybdates and heteropolytungstates appear to contain predominantly one distinct species of anion. It is generally reasonable to assume that this predominant species is identical with the anion existing in the solid state, in equilibrium with the solution, or is closely related to it ; some heteropolyanions are remarkably stable.

Basicity and acid strength: Heteropolyacids and salts are not stable in aqueous medium and undergo partial hydrolytic degradation to produce H^+ ions but these can be stabilized in mixed solvents such as water-dioxane, water-acetone, water-alcohol, etc.Heteropolytungstates are more stable in aqueous medium than the corresponding molybdates. 12-Heteropolymolybdates with different heteroatoms differ markedly in their stability to degradation in water solution in the following decreasing order

Si > (Zr, Ti) > Ge > P > As

The pH range of stability extends highest for heteropolycompounds containing Si as the heteroatom while very acidic solutions are required to keep the 12-heteropolymolybdates with phosphorus as the central atom intact as 12-anions.

8. Thermal stability of the free acids of the heteropolymolybdates and heteropolytungstates is quite high. The stability is dependent on the nature of the heteroatom and addenda atom. Complexes containing phosphorous as the central atom are generally more stable than the compounds containing silicon as the heteroatom. Heteropoly compounds containing tungsten as the addenda atom are more stable than those with molybdate atoms. The decomposition at high temperatures causes loss of acidity. The phosphomolybdic acid gets decomposed to the corresponding MoO_3 and P_2O_5. The Keggin structure is reconstructed when the complex is exposed to an atmosphere containing water vapour whereas in the case of less labile polyoxotungstates this kind of reconstruction is less likely. Heteropolyacids are used as solid acid catalysts for vapour phase reactions at high temperatures. The substitution of transition metals in the anionic framework generally reduces the thermal stability in these complexes. The substitution of molybdenum in phosphomolybdic acid by addenda atom/s such as vanadium reduces the thermal stability of the resulting phosphomolybdovanadates. The thermal stability reduces with the vanadium atoms in the polyanion framework. At higher temperature there is eviction of vanadium from the primary structural framework and the subsequent degradation into simple oxides i.e., MoO_3 and V_2O_5. The formation of such species is detected by X-ray diffraction analysis which clearly distinguishes between the heteropoly and the metal oxide phases. The structure of such complexes can be reconstructed on exposure to atmosphere of water vapour.

1.6 Synthesis of Keggin heteropoly compounds

1.6.1 Synthesis of the free acid series

The heteropoly compounds of the free acid kind are commercially available in very pure state as crystalline hydrates. Heteropolyacids are generally prepared by acidifying an aqueous solution containing the salt of the heteroelement and alkali metal molybdate and tungstate. The product as the free acid is then isolated by extracting with ether or by ion exchange technique. As a rule, the yields obtained are not high, involving a large amount of waste products formed in the process [3]. Tungstophosphoric acid is formed in the following manner

$12WO_4^{2-} + HPO_4^{2-} + 23H^+ \rightarrow PW_{12}O_{40}^{3-} + 12\ H_2O$

The equilibrium constants and rates of formation are large enough to allow the polyanions to be crystallized as salts from stoichiometrically acidified mixtures of the components at room temperature. A careful control of pH and temperature may be necessary during the synthesis. The sequence of addition of the reagents may also play an important role, for e.g.,

SiO_3^{2-}, WO_4^{2-} then $H+ \rightarrow \alpha\text{-}[SiW_{12}O_{40}]^{4-}$

WO_4^{2-}, H^+ then $SiO_3^{2-} \rightarrow \beta\text{-}[SiW_{12}O_{40}]^{4-}$

Acidification is achieved by the addition of common mineral acids. The members of the free acid series are sufficiently stable to be crystallized from aqueous solution. In such cases the anions can be isolated from the reaction mixture by the "etherate" method. When a strongly acidified solution of the heteropolyanion is shaken with excess of diethyl ether, three phases separate out (a) an upper ether layer (b) an aqueous layer and (c) a heavy oily etherate layer. The heavy oily etherate layer is then drawn off, shaken with excess ether to separate entrained aqueous solution, and separated again. The etherate is decomposed by the addition of water, the ether is removed, and the aqueous solution of the heteropoly acid is allowed to evaporate until crystallization is accomplished. Exact nature of the etherate is not clear although Et_2OH^+ group has been detected by infrared spectroscopy. During the synthesis of $H_3PMo_{12}O_{40}$ by this technique the etherate of the acid is reported to contain approximately 20 mol ether and 50 mol water per mol of heteropolyacid. Isolation of the polyanions from solution is generally achieved by the addition of an appropriate counter cation such as salts of alkali metal, ammoniun or the tetra alkyl

ammonium series. Salts of larger alkyl ammonium and similar cations such as tetrabutyl ammonium, etc., are insoluble in water but can be recrystallized from solvents such as acetonitrile, nitromethane and acetone. Another method for the synthesis of heteropolyacids is electrodialysis. An efficient electromembrane technique is used for the synthesis of phosphotungstic acid which is among the most important acid catalyst in the HPA series. The heteropolyacid is formed in the anode compartment of the dialyzer from Na_2WO_4 and H_3PO_4 in an aqueous solution. Acidification is achieved by the electrolysis of water. Sodium ions are transferred by the electric potential from anode to the cathode through a cation–exchange membrane. Thus pure tungstophosphoric acid is formed at the anode and sodium hydroxide at the cathode. The alkali thus obtained can be used to prepare sodium tungstate from starting WO_3. The heteropolyacid prepared by this method is obtained in pure form with no waste material formed. Many a transition metal containing heteropolyanions can also be obtained by this technique [4].

1.6.2 General methods of preparation of transition metal substituted polyoxometalates (TMSP)

The TMSP is a general name for transition metal substituted polyoxometalates which contain transition metals as addenda ions. The common transition metals incorporated in the framework are the first row metals. The transition metal fits into the lacunary vacancy created in the otherwise complete Keggin structural unit. The lacunary or “defect structure” is created by the loss of an MO_6 octahedra (which is equivalent to stoichiometric loss of an MO^{n+} unit resulting in the formation of $XM_{11}O_{39}^{n-}$). This involves the partial degradation of the Keggin unit by lowering the pH of the solution by the addition of a suitable buffer. The pH is dependent on the nature of the central and the addenda atom. The solubilities of the TMSP complexes can be controlled by selecting an appropriate counter cation. Usually alkali metals and tetra alkyl ammonium groups are the counter cations of choice. There are two methods for the synthesis of TMSP. The first method (method A) involves the addition of a transition metal salt to the already prepared isolated lacunary salt under appropriate synthetic conditions while the second method (method B) developed by Simmons *et al* involves the generation of *in situ* lacunary vacancy followed by the addition of the transition metal salt.

1.6.2.1 Method A

Preparation of lacunary polyoxometalates

The lacunary heteropolyanions usually prepared are the sodium or the potassium salts of $PW_{11}O_{39}^{7-}$ or $SiW_{11}O_{39}^{8-}$ .The aqueous solution of the transition metal salt is added to either Na / K salt of either $PW_{11}O_{39}^{7-}$ or $SiW_{11}O_{39}^{8-}$ with an appropriate molar ratio followed by the addition of sodium carbonate to attain the needed pH values depending on the nature of the elements in the anionic framework

Preparation of $K_7[PW_{11}O_{39}] .xH_2O$

Tungstophosphoric acid is dissolved in hot water and a concentrated potassium acetate solution (with pH adjusted to 7 with acetic acid) is added drop wise under vigorous stirring. The reaction mixture is then filtered and the filtrate refrigerated. The precipitate obtained is filtered and dried in a desiccator over silica gel [5].

Another method for the preparation of same compound is as follows. Tungstophosphoric acid is dissolved in hot water and solid potassium chloride is added to this solution. The pH of this solution is adjusted to 5 by the addition of aqueous solution of 1M potassium bicarbonate. After some time the reaction mixture is filtered through a membrane filter. The filtrate is then concentrated and allowed to stand at room temperature. White crystalline salt that forms is separated and recrystallized from hot water [6].

Preparation of $Na_7[PW_{11}O_{39}].xH_2O$

Sodium tungstate and disodium hydrogen phosphate are dissolved in water. The solution is heated upto 80-90 ^{o}C and titrated with concentrated nitric acid with stirring till the pH reaches 4.8. The volume of the solution is then reduced to half by evaporation and then the HPA is separated in a dense lower layer by liquid – liquid extraction with acetone. The process is repeated till the acetone extract shows no nitrate ions. The sodium salt is obtained as the hydrate by evaporation to dryness (in air) of the acetone extracts [7].

Preparation of $K_8[SiW_{11}O_{39}].xH_2O$

Sodium tungstate and sodium silicate is dissolved in hot water. Progressively 4 M HCl is added while maintaining at boiling temperature for one hour. The potassium salt is obtained by the addition of solid potassium chloride [8].

Preparation of TMSP

Aqueous solution of a slight excess of transition metal salt such as Co, Mn, Fe, Ni etc. (as chloride, nitrate or acetate) is added to the aqueous solution of the lacunary species. The resulting solution is then buffered depending on the nature of the metal incorporated. The potassium salt is then isolated by the addition of potassium chloride. The complex containing sodium ions as the counter cation is prepared by the addition of the sodium salt of the lacunary compound to the transition metal salt and subsequent adjustment of the pH by the addition of a suitable buffer [9].

1.6.2.2 Method B

In this method the lacunary vacancy is created *in situ* in the Keggin unit by the addition of transition metal salt under appropriate pH conditions [10]. The $XM_{12}O_{40}$ anion is partly degraded *in situ* to the lacunary $XM_{11}O_{39}$ species by the addition of buffer such as potassium acetate or potassium bicarbonate to adjust the pH depending on the nature of the central and the neighbouring addenda atoms as shown in the table below

Heteroatom	Addenda Atom	pH needed
P, Si, Ge	Mo	4.3- 4.5
P	W	5.0 -5.5
Si, Ge	W	6.0-6.7

The hydrated silicotungstic acid is dissolved in water containing acetic acid. The pH is adjusted to a pH 6.0-6.7 by the addition of the buffer, potassium acetate. The solution is then boiled and to which is added aqueous solution of cobalt acetate. This is followed by the addition of solution of potassium acetate containing glacial acetic acid. This hot solution is then filtered and the filtrate kept at 5°C overnight for the separation of the product to yield $K_6[SiW_{11}Co(H_2O)O_{39}].nH_2O$

1.6.3 Preparation of mixed addenda heteropoly compounds

The mixed addenda complexes are formed by the substitution of one or more tungsten (VI) or molybdenum (VI) ions in the Keggin structure by other addenda atom like tungsten (VI), molybdenum (VI) and vanadium (V). By changing the number and the kind of substituted addenda and the heteroatoms, numerous mixed addenda heteropolyanions can be prepared and applied as catalysts for oxidation reactions. The mixed addenda complexes containing phosphorus, molybdenum and vanadium are among the most widely used because of their oxidizing ability attributable to the high value of oxidation potential. The methods of preparation of molybdovanadophosphates with protons, alkali metals and tetra alkyl ammonium groups as the counter cations are described in detail.

1.6.3.1 Synthesis of molybdovanadophosphoric acids

This class of mixed addenda contains protons as the counter cations. In this series of heteropolyacids the molybdenum atom(s) are substituted by vanadium atoms. These compounds are prepared by two methods. In the first method, Tsigdinos and Hallada prepared H_{3+x} $[PMo_{12-x}V_xO_{40}]$. n H_2O (where x = 1, 2, 3) by mixing the aqueous solutions of $Na_2HPO_4.12H_2O$, $NaVO_3$ and $Na_2MoO_4.2H_2O$ in appropriate molar ratio in acidic medium [11].

The heteropolyacids formed were extracted with diethyl ether and recovered by evaporation of the ether layer. The resulting orange coloured powdered were recrystallized from water and the crystals were dried in air and stored over silica gel in a desiccator.

The second method involves dissolving MoO_3 and V_2O_5 with stoichiometric amount of phosphoric acid in water and refluxing the resulting solution [12].

$H_3PO_4(aq) + (12-x)MoO_3 + x/2\ V_2O_5 + x/2H_2O \rightarrow H_{3+x}\ PMo_{12-x}V_xO_{40}$

This method introduces only the essential components into the solution but works only at low vanadium contents. The dissolution of vanadium pentoxide is very slow into the polyoxometalate system which requires long refluxing times extending upto one week. Synthesis of $H_4[PMo_{11}VO_{40}]$ proceeds with complete incorporation of vanadium pentoxide. The V_2O_5 incorporation remains incomplete even after prolonged hours of refluxing. The vanadium pentoxide incorporation becomes more difficult with increasing vanadium content so this method is disadvantageous for systems having compositions with $x \geq 3$

1.6.3.2 Molybdovanadophosphates with alkali metals as the counter cations

Synthesis of sodium salt of molybdovanadophosphates involves the mixing of the aqueous solutions of molybdovanadophosphoric acid and sodium hydrogen carbonate in appropriate molar concentrations and subsequent drying of the obtained solid [13].

The aqueous solution of the sodium salt is obtained in the following manner

Since the solubility of MoO_3 in acidic solution is more than that of V_2O_5, the MoO_3 is reacted with a dissolved vanadate salt with stoichiometric quantities of H_3PO_4 to directly obtain the partial salt solutions. Thus $NaVO_3$ (a dissolved vanadate salt) is prepared in the same pot by dissolving V_2O_5 with stoichiometric quantities of Na_2CO_3.

$V_2O_5 + Na_2CO_3 \rightarrow 2\ NaVO_3(aq) + CO_2$

$$H_3PO_4(aq) + (12\text{-}x)MoO_3 + x\,NaVO_3(aq) \rightarrow Na_xH_3\,PMo_{(12\text{-}x)}V_xO_{40}(aq)$$

This method provides a rapid, scalable, one pot synthesis. The reaction can be accomplished within half a day in the laboratory [12].

1.6.3.3 Molybdovanadophosphates with alkyl ammonium groups as the counter cations

Synthesis of the ammonium salt is carried out by mixing the appropriate molar ratios of aqueous solutions of the corresponding free acids and ammonium chloride followed by subsequent drying of the obtained precipitate[11].

The tetrabutyl ammonium salts are prepared by two methods [14]. The first method includes the direct addition of excess tetrabutyl ammonium bromide to the aqueous solution of the molybdovanadophosphoric acid and drying of the yellow coloured precipitate.

The second method involves the *in situ* generation of the lacunary $PMo_{11}O_{39}{}^{7-}$ into which the vanadium is incorporated followed by the addition of tetrabutyl ammonium bromide. To the aqueous solution of $H_3[PMo_{12}O_{40}]$ is added solid lithium carbonate until the pH reaches 4.3. A single peak at δ -1.39 ppm (^{31}P NMR) confirms the presence of pure form of a lacunary species. To this solution is added aqueous solution of $NaVO_3$ (dissolved at 90^oC) and cooled to room temperature. The clear orange solution is adjusted to pH 0.5 with 6M HCl and then stirring is continued for 48 hours. To the solution is added solid tetrabutyl ammonium bromide. The immediately produced yellow powder is then stirred with water for 5 hour and filtered off, washed again with water, then with ethanol and finally with ether in vacuo.

1.7 Catalytic activity of heteropoly compounds

Heteropolyacids have several advantages as catalysts which make them economically and environmentally attractive and viable. On one hand heteropolyacids have a very strong Bronsted acidity approaching the superacid region on other hand they are efficient oxidants exhibiting fast reversible multielectron redox transformations under mild reaction conditions. Solid heteropolyacids have a discrete ionic structure comprising of fairly mobile basic structural units- anions and the counter cations. This unique structure manifests itself to exhibit an extremely high proton mobility and " pseudoliquid phase" while the heteropolyanions are useful in the stabilization of cationic organic intermediates. Other attractive properties like high solubility in polar solvents, and a fairly high thermal stability in the solid state render them as potentially promising acid catalysts [15].The substitution of one or more of the addenda atoms in the Keggin anionic framework by other transition metal increases the oxidation properties of the heteropoly compounds. The transition metal substituted compounds are active as oxidation catalysts with a wide range of organic / inorganic substrates and are operable with a wide variety of oxygen donors in various solvents [16].

Acid catalysis in heteropolyacids

The property of acid catalysis in the heteropolyacids is attributed to the strong Bronsted acidity which is found superior to the the acid catalysts like mineral acids. In contrast to the mineral acids the heteropolyacids are non-toxic, non-volatile, have no smell and are stable to prolonged storage. Although heteropolyacids are found to be more expensive than the mineral acids their use is justified due to their high efficiency and selectivity exhibited in catalytic reactions. Acid catalysis by heteropolyacids proceeds under mild reaction conditions. Due to the inert nature of the anions they do not enter into side reactions like chlorination, sulphonation and nitration as observed in mineral acids. The acid strength of the heteropolyacids is found to be greater than that of the mineral acids as described earlier. In the case of heteropolyacids the negative charge of similar value is spread over much larger anions than those formed from mineral acids, thus the electrostatic interaction between the protons and anions is much less for heteropolyacids (allowing easy dissociation of protons) than the mineral acids. There is weak dependence on the acid strength of the heteropolyacid on their composition. This is due to the large size of the heteropolyanion and the unusual proton structure of the heteropolyacid. In aqueous and non aqueous-solutions the heteropolyacid consists of solvate separated ion-pairs $H^+(H_2O)_m$ // HPA $^{n-}$ in which the protons are hydrated and linked to the anion as a whole and not to a specific centre in heteropolyanion. The HPA structure consists of a charged sphere with a large radius on the surface of which the acid protons are accommodated in the form of point charges. In general the acid strength increases with a decrease in the negative charge of the anion or the an increase in the valency of the hetero atom [2]

Co < B < Si, Ge < P

The general trend in acid strength is as follows [15]

$H_3PW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4SiW_{12}O_{40} \cong H_4GeW_{12}O_{40} > H_4SiMo_{12}O_{40} > H_4GeMo_{12}O_{40}$

The acidity of heteropolytungstates is more than that of the heteropolymolybdates which agrees with the higher negative charge on the oxygen atom in heteropolymolybdates compared to that of the heteroplytungstates. Thus the tungstophosphoric acid are the most widely used compared to the other acids because of their higher acidity, hydrolytic and thermal stability and lower oxidation potential compared to molybdenum and vanadium containing heteropolyacids. The acid strength, number of acid centers as well as the related properties of the heteropolyacids can be controlled by varying the structure, compositon of the heteropolyanions, the extent of hydration, nature of support and the thermal treatment rendered to the HPA.

Acidity in salts

Sometimes the protons in heteropolyacids are replaced by alkali and transition metals. This increases the surface area for e.g., if the protons in $H_3PW_{12}O_{40}$ are replaced by a large atom like cesium the surface area increases from < $10m^2/g$ for the acid to ≅ 130 m^2/g for the cesium salt. There are several possible types of origins of acidity in the heteropoly salts [2]

(a) dissociation of coordinated water

$$Ni(H_2O)_m^{2+} \rightarrow Ni(H_2O)_{m-1}(OH)^+ + H$$

(b) Lewis acidity of metal ion.

(c) protons formed by the reduction of metal ions for eg., $Ag^+ + ½H_2 \rightarrow Ag^o + H^+$

(d) protons present in the acidic salts for example as in $Cs_xH_{3-x}PW_{12}O_{40}$

(e) partial hydrolysis during the preparation process for example

$$PW_{12}O_{40}^{3-} \rightarrow PW_{11}O_{39}^{7-} + WO_4^{2-} + 6H^+$$

Supported heteropolyacids

Acids such as tungstophosphoric acids when supported on inorganic carriers like silica reduces the acid strength. The acid strength of tungstophosphoric acids diminishes inthe following sequence of supports SiO_2 > Al_2O_3 > activated charcoal.The acid strength of the heteropolyacids on SiO_2 as measured by ammonia TPD (thermal programmed desorption) decreases in the order$H_3PW_{12}O_{40}$(865 K) > $H_4SiW_{12}O_{40}$ (805 K) > $H_3PMo_{12}O_{40}$ (736 K) > $H_3SiMo_{12}O_{40}$ (696 K). The values in brackets are the temperatures of desorption [2].

Determination of acid strength in heteropolyacids

Thermal desorption of basic molecules like pyridine and ammonia reveals the acidic properties. Pyridine adsorbed on SiO_2-Al_2O_3 is completely desorbed at 573 K. On the other hand sorbed pyridine in $H_3PW_{12}O_{40}$ mostly remains at 573 K, indicating that the heteropoly compound is a very strong acid. Ammonia adsorbed on SiO_2-Al_2O_3 is mostly desorbed at temperatures less than 800 K, while $H_3PW_{12}O_{40}$ gives a relatively sharp peak at about 800 K. The acidity is also determined by the Hammett function which is then compared to the values for mineral acids [2].

1.7.1 Applications as acid catalysts

The high acid strength of heteropolyacids makes them excellent catalysts for a wide variety of acid catalyzed reactions. Literature is rich in reports with the utility of heteropoly compounds as acid catalysts [15]. In acid catalysis the Bronsted acidity plays an important role. Heteropolyacids are active catalysts in solution compared to the conventional catalysts such as the mineral and organic acids. These are used as industrial catalysts for several liquid phase reactions. The important characteristics accounting for the high catalytic activity include the acid strength, softness of the heteropolyanions, catalyst concentration and the nature of the solvent. Molar catalytic activity of heteropolyacids is often 100-1000 times higher than that of mineral acids. Thus it is possible to carry out the catalytic process at a lower catalyst concentration and at a lower temperature. There are no side reactions observed with the heteropolyacids. Heteropolyacids are successfully used in the industry as heterogeneous catalyts for liquid-phase reactions. Advantages of heterogeneous catalysts include easy separation and reuse. Use of heteropolyacids on inoganic carriers has been a field of growing interest. Supports such as silica, alumina, titanium oxide are widely used for heterogeneous reactions. Recent reports include the use of mesoporous molecular sieves such as MCM-41 as supports for heteropolyacids for acid catalyzed reactions.

1.7.1.1 Heteropolyacids for homogeneous liquid- phase acid catalyzed reaction

1. Hydration and Dehydration reactions

The hydration of propylene was the first commercial process based on heteropolyacid catalysis. The activity of the aqueous solution of $H_3PW_{12}O_{40}$ is found to be two or three times more than that of sulphuric or phosphoric acid by Misono *et al*. The basic reason for high selectivity is assumed to be stabilization of the intermediate propyl cation by coordination by the heteropolyacids [17].

Izumi *et al*. observed high activity of heteropolyacids for the hydration of isobutene in dilute solutions. The activation energy is 4 kcal mol^{-1} lower for $H_3PW_{12}O_{40}$ than for nitric acid. This is a commercial process for the separation of isobutene from a mixture of isobutene and n-butene through a direct hydration of the former to give tert- butyl alcohol [18-22].

Matsuo et al have found that heteropolyacids have an edge as catalysts over H_2SO_4 and $HClO_4$ in the hydration of phenyl acetylene [23].

Higher activities of heteropolyacids are also found by Baba *et al* for the dehydration of 1,4-butanediol to yield tetrahydrofuran [24]. The activity is in the order

$H_4SiW_{12}O_{40} > H_3PW_{12}O_{40} > H_3PMo_{12}O_{40}$

2. Prins Reaction

Urabe and his group have carried out Prins reaction of alkenes, which proceeds with $H_3PW_{12}O_{40}$ as catalyst and is found be 10-50 times more active than sulphuric or para toluene sulphonic acid (PTS) [25].

3. Ether cleavage reaction

Heteropolyacids are both active and selective catalysts in the homogeneous alcoholysis of epoxides such as epichlorohydrin, 1,2- epoxybutane, isobutene oxide and styrene oxide under mild reaction conditions (45^{o}C and excess of alcohol) as shown by Izumi *et al* . The $H_3PW_{12}O_{40}$ shows a higher activity for the above reaction compared to sulphuric, para toluene sulphonic acid or perchloric acid. While rapid deactivation is observed with sulphuric acid probably due to the formation of alkyl sulphate, $H_3PW_{12}O_{40}$ maintains its activity [26, 27].

4. Polymerization of tetrahedydrofuran (THF)

The heteropolyacid, $H_3PW_{12}O_{40}$ is used by Izumi *et al* for the preparation of polyoxotetramethylene glycol (PTMG) which is employed for the manufacture of spandex fibres and polyurethanes. PTMG is commonly prepared by a two step process i.e., ring opening followed by hydrolysis [26].

Aoshima *et al* found that THF can be directly polymerized to give PTMG in a highly concentrated solution of $H_3PW_{12}O_{40}$ [28].

5. Condensation Reaction

Cyclotrimerization of propionaldehydehas been performed by Khankhasaeva *et al* to give 2,4,6-triethyl- 1,3,5 trioxane catalyzed by $H_3PMo_{12}O_{40}$. Selectivity exceeding 97 % and turn over exceeding 300 moles of product per moles of catalyst have been obtained.

Condensation of acetone to give mesitylene is catalyzed by $H_3PW_{12}O_{40}$ at room temperature [39]. Kozhevnikov and his research group catalyzed the condensation of isophytol with 2,3,5- trimethyl hydroquinone to yield α- tocopherol which is the active form of vitamin E using $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ as the catalyst [30].

6. Methyl Tertiary Butyl Ether (MTBE) synthesis

MTBE is a gasoline octane booster which is produced industrially on a large scale by reacting isobutene with methanol in the presence of acidic ion-exchange resin.Heteropolyacids and their salts were found to catalyze the above reaction in homogeneous and heterogeneous reaction conditions by Ono and co workers [31].

Keggin type heteropolyacids were shown to be 2-4 times more active as catalysts by Maksimov et al than the conventional acid catalysts with respect to reaction rate per unit proton site [32].

7. Esterification and ester decomposition

The reaction of carboxylic acids with olefins proceeds in solution in the presence of $H_3PW_{12}O_{40}$ at the concentration level of $10^{-4} – 10^{-2}$ mol dm^{-3} at 293- 413 K with 100% selectivity. The esterification of p-nitrobenzoic acid with ethanol was performed by Ono, Kozhevnikov and others with 3-7 wt % $H_3PW_{12}O_{40}$ at 75°C [33, 34].

The synthesis of dialkyl phthalates used as plasticizers was achieved by Schwegler and his team after esterifying phthalic anhydride with C_8-C_{10} alcohols at 100-120°C in the presence of $H_3PW_{12}O_{40}$ [35].

8. Alkylation

Alkylation of hydroquinone with isobutene to yield 2- tert – butyl hydroquinone and 2,5–di- tert-butyl hydroquinone is catalyzed with $H_3PW_{12}O_{40}$ by Timofeeva *et al* under phase transfer conditions in biphase system including toluene (upper phase) and HPA dioxane etherate (lower phase). The products are obtained from the toluene phase [36].

9. Other reactions include Beckmanns rearrangement and Pinacol rearrangement [37,38].

1.7.1.2 Heteropolyacids as heterogeneous catalysts

Reactions in liquid- solid system are catalyzed by bulk and supported heteroplyacids and their salts. Advantage of this category of acid catalysts is their easy separation from the reaction mixture.

1. Dehydration and hydration reaction

$H_3PW_{12}O_{40}$ was found to be more active catalyst by Hayakawa *et al* for the dehydration of 2-propanol than SiO_2-Al_2O_3 at 398 K [39]. The unique activity of the cesium salt of $H_3PW_{12}O_{40}$ was found by Tatematsu and his team for the dehydration of 2-propanal. The high activity is explained by the pseudo liquid behaviour of $H_3PW_{12}O_{40}$ and its affinity for polar molecule like 2-propanol [40].

Bulk and supported heteropolyacids like $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ are proven to be active catalysts for the hydration of isobutylene by Baba *et al* [41]. Various supports have been tried for this reaction which include Amberlyst 15 [porous sulphonated poly (styrene-divinylbenzene)], activated carbon, silica and titanium oxide. Maximum activity is observed when Amberlyst 15 is used as the support at 30 wt % $H_4SiW_{12}O_{40}$.

2. Esterification and ester decomposition

Activated carbon entraps $H_3PW_{12}O_{40}$ and exhibits catalytic activity for the esterification of acetic acid with ethanol. The activity is more compared to Nafion-H. The selectivity to ethyl acetate was found to be 99.5% by Izumi and co workers at 95 % conversion with HPA [42]. Ceasium salt of $H_3PW_{12}O_{40}$ was found to be more active as catalyst by Okuhara for the decomposition of cyclohexyl acetate in solid- liquid mixture than other acid catalysts like Nafion-H, HY zeolite, HZSM-5, SiO_2- Al_2O_3 and sulphonated zirconia as the ceasium salt has a much larger surface area [43].

3. Alkylation and Dealkylation

Soeda *et al* have carried out catalytic monoalkylation of hydrocarbons like p-xylene with isobutene and with $H_3PW_{12}O_{40}$ as the catalyst with 75 % selectivity.The product tertiary butyl para- xylene is an important precursor for liquid crystalline polyesters and polyamides with low melting point and good solubility [44].

Alkylation of para-cresol by isobutene was performed by Kozhevnikov for the synthesis of phenolic antioxidants. The activity of $H_3PW_{12}O_{40}$ is greater by four orders of magnitude than sulphuric acid [45].

$H_4SiW_{12}O_{40}$ on SiO_2 is an excellent catalyst for the alkylation of benzene with1-dodecene at room temperature as shown by Izumi et al [46].

Dealkylation reactions are also performed with solid HPAs. Thus dealkylation of 2,6 -di-tert- butyl phenol takes place at 403-423 K in the presence of solid $H_3PW_{12}O_{40}$. The heteropolyacid was found to be two orders of magnitude more active than $Al_2(SO_4)_3$ for this reaction by Kulikov *et al* [47].

1.7.2 Heteropoly compounds in oxidation catalysis

Oxidation catalysis by polyoxometalates especially by the Keggin type heteropoly oxometalates is a rapidly expanding area due to their unusual versatility and compatibility with environmentally friendly conditions (with oxidants like O_2 and H_2O_2) and operations. The research in the area of oxidation using this category of complexes has been intense in the past decade for several reasons (a) oxidation reactions are challenging in nature in order to achieve satisfactory yields and high selectivity levels (b) the existing catalytic processes leave ample margin for further improvement to develop new catalyst system that can perform under rigid reaction conditions (c) the reaction mechanisms are quite complex for oxidation reactions and even multiple mechanisms can be simultaneously operable (d) extensive application in areas ranging from fine chemical synthesis to the degradation of many toxic materials .Substitution of the addenda atom/s by either d electron transition metal (TMSP) or other addenda atoms increases the oxidation ability of the heteropolyoxometalate. The synthesis of the TMSP complexes was attempted after a thorough study of the metalloporphyrin system by Hill and his group. This TMSP system was to behave as oxidation catalyst by transferring oxygen from a typical donor to the organic substrate.

TMSP complexes show many of the attractive features exhibited by metalloporphyrins ability for dioxygen binding (b) formation of high valent species with stoichiometric oxygen transfer (c) reaction with oxidants such as iodosobenzene, sodium periodate and tertiary butyl hydroperoxide (d) these multidentate ligand systems can bind the *d* electron transition metal ion in multiple oxidation states with sufficient strength so that they are not lost from the structure. This is critical as the oxidation process brings about a change of oxidation state in the metal. The change in the oxidation state results in sufficient change in lability and other electronically controlled properties and hence it is often difficult for the ligand system to retain the metal in the framework structure during the catalytic cycle. If during the oxidation process structural degradation of the catalyst takes place the metal atom is lost as it is precipitated as the metal oxide. These metal oxides are suitable as catalysts only under heterogeneous conditions and are inactive for low temperature homogeneous reaction conditions (e) both complexes can activate substrates in proximity to the active site (f) metalloporphyrins and the TMSP systems can be reduced which facilitates the activation of some oxidants and the quenching of various intermediates observed in the process of oxidation (g) the electronic structure can be altered and controlled by rational synthesis and (h) both the catalytic systems can be rendered soluble in polar and non-polar media. The TMSP complexes have an edge over the metalloporphyrin system as catalyst for oxidation. The metalloporphyrins are organic molecules and are thermodynamically unstable in the presence of strong oxidizing agents and hence undergo oxidative degradation during the reaction. The TMSP complexes are not susceptible to oxidative degradation and hence continue to catalyze the oxidation reaction for a longer period than metalloporphyrin and other inorganic complexes with organic ligands. They are thermally more robust than the porphyrin and other macrocyclic ligands. The acceptor properties of the oxometalate ligands are dependent on its reducibility and can be modified by metal replacement or partial reduction. The electron population on metal and and ligand is more variable as compared to the metalloporphyrins. The TMSP complexes unlike metalloporphyrins are readily accessible and available in significant levels in two-three step synthesis. Solubility, an important aspect for homogeneous catalysis can be easily controlled by judicious choice of the counter cations during synthesis of the TMSP complexes. In these complexes the transition metal is bound by an inorganic ligand, the lacunary polyoxometalate which acts as the multielectron acceptor.

Mixed addenda comlpexes are those in which one or more of the addenda atoms in the framework are substituted by other addenda type atoms like tungsten, molybdenum or vanadium. The attractiveness of this class of compound as catalysts for oxidation is their high value of oxidation potential, low cost, thermal stability and oxidative robustness, ease in preparation and solubility in media ranging from water to hydrocarbons. The redox potential depends on (a) negative charge density and (b) elemental composition. Both the factors can be controlled to a great extent synthetically. The dependence of redox potential on elemental composition is dictated by the presence or absence of the most oxidizing addenda metal atom.

The order of decreasing redox potentials are V(V) >Mo(VI)> W(VI).

Hence the molybdovanadophosphate system is the most extensively studied for oxidation reactions. Thus all the types of Keggin compounds mentioned above are found to be compatible in operation with environment friendly oxidants like oxygen and hydrogen peroxide. They are also found to be reactive with oxidants like tertiary butyl hydroperoxide, iodosobenzene, sodium periodate, potassium persulphate, etc.

1.7.2.1 Oxidation with molecular oxygen

Oxidation with molecular oxygen heteropolyoxometalate facilitated oxygen activation is applied to a wide range of organic substrates. Oxidation by molecular oxygen is influenced by the oxidation potential of the TMSP. The TMSP of the Keggin type are efficient oxygen binders. They act as catalysts by oxygen transfer from a typical donor to a typical TMSP followed by transfer of this TMSP activated form of oxygen to an organic substrate.

The TMSP complexes are potential catalysts for the epoxidation of olefins in the presence of aldehydes in the presence of molecular oxygen or air as the oxidant. Mizuno et al have found pronounced catalytic activity of $PW_{11}CoO_{39}^{5-}$ for the epoxidation of alkenes such as cyclohexene, 1-decene and styrene by molecular oxygen in the presence of aldehydes such as isobutyraldehyde and pivaldehyde at 303 K [48].

Alkene epoxidation by dioxygen in the presence of isobutyraldehyde and the tetrabutyl ammonium salts of transition metal substituted heteropolyanions $PW_{11}MO39^{n-}$ ($PW_{11}M$;M = Co^{II}, Mn^{II}, Cu^{II}, Pd^{II}, Ti^{IV}, Ru^{III}, V^{V}) has been studied by Kholdeeva et al. Trans-stilbene is used as the model substrate in acetonitrile medium. Selectivity of epoxidation reached 95% at complete alkene conversion. The reaction is shown to be inhibited by 2,6- di-tert-butyl- 4-methyl phenol indicating chain radical mechanism for this reaction. The acyl peroxy radical is found to be the active species for epoxidation [49].

Selective epoxidation of cyclohexene by mono-transition metal substituted Keggin type heteropoly tungstates by molecular oxygen in the presence of aldehyde has

been reported by Mizuno *et al*. The substituted transition metals are cobalt, copper, iron, nickel and manganese. The epoxidation of 1-decene and styrene was reported with $PW_{11}CoO_{39}^{5-}$ as the catalyst. This reaction might involve peracids as intermediates as the formation of perisobutyric acid is confirmed by ^{1}H NMR [50]. Oxidation of olefins and ketones by molecular oxygen / aldehyde / vanadium heteropolyoxometalate system has been achieved by Hamamoto *et al*. Olefins were epoxidized with dioxygen in the presence of two equivalents of 2- methyl propanal under the influence of catalytic amounts of $(NH_4)_6[PMo_6V_6O_{40}]$ to give the corresponding epoxides in moderate to good yields. This system was also extended to allylic and homo allylic alcohols. Baeyer–Villiger oxidation of cyclic ketones was achieved using benzaldehyde instead of 2-methyl propanal [51].

Kuznetsova *et al* found that $PW_{11}Fe(H_2O)O_{39}^{5-}$ in the pH range 3.5-5 at 20°C is an active catalyst for H_2S oxidation with O_2 to elemental sulphur [52].

Harrup *et al* discovered that the polyoxometalate based catalysts such as $K_5[Zn PW_{11}O_{39}]$, a - $K_8[SiW_{11}O_{39}]$, a -$K_6[Zn SiW_{11}O_{39}]$ and $K_4[NaP_5W_{30}O_{110}]$ are active for the aerobic oxidation of H_2S to elemental sulphur at 60°C and under 1.1 atm of O_2 [53].

Chromium(III) heteropolytungstate or their corresponding oxygenated form, oxo Cr (V) are efficient as catalysts for the oxidation of alkenes, alkanes, alcohols and triphenylphosphines by a variety of oxidants such as OCl^-, H_2O_2 or PhIO. Khenkin and Hill thus oxidized alkenes to epoxides, allylic alcohols, ketones and Cr(III) by oxo Cr(V) complexes [54]. Thus

$$Cr^{V} = O + \text{Substrate} \rightarrow Cr^{III} + \text{Substrate O}$$

Kuznetsova *et al* prepared the complexes of Pd(II) and Pt(II) with $PW_{11}O_{39}^{7-}$ and these heteropolyanions were found to be catalytically active for the oxidation of benzene to phenol. The reactions were performed in a mixture of O_2 and H_2 gases in a two phase water- benzene system at a temperature of 10-40°C [55].

Passoni and fellow workers made the use of heteropolyacids as reoxidants for Pt in the direct oxidation of benzene to phenol with molecular oxygen. The conversion with respect to benzene was about 15 % and the selectivity to phenol was about 70 % [56].

Phenol synthesis by liquid phase oxidation of benzene with molecular oxygen over iron heteropolyacids was studied by Y-J Seo *et al* [57].

The vanadium substituted heteropolyanions have a fairly high value of oxidation potential (0.7 V relative to NHE) and are capable of oxidizing substrates ranging from organic to inorganic compounds. They are reversibly acting oxidants i.e., their reduced forms can be reoxidized to the original form by oxygen in mild conditions. The $V^{4+} \leftrightarrow V^{5+}$ transformation is actually responsible for the redox activity of mixed addenda heteropolyacids [15].

Neumann *et al* have successfully carried out the oxidative dehydrogenation of α-terpinene to p-cymene catalyzed by mixed addenda compound of the type $H_5[PMo_{10}V_2O_{40}]$. The reaction mechanism involves the formation of a stable substrate catalyst complex in the catalyst reduction (substrate oxidation state) stage and the formation of a μ- peroxo catalyst intermediate in the catalyst reoxidation stage [58].

$$\text{Substrate} + \text{Catalyst}_{ox} \rightarrow \text{Product} + \text{Catalyst}_{red} + 2H^+$$

$$\text{Catalyst}_{red} + 2H^+ + \tfrac{1}{2}O_2 \rightarrow \text{Catalyst}_{ox} + H_2O$$

Oxidation of trialkyl substituted phenols like 2,3,6-trimethyl phenol in the presence of phosphomolybdovanadium heteropolyacids has been reported by Kholdeeva et al. The product obtained is 2,3,5-trimethyl-1,4-benzoquinone with 86 % yield and 100 % conversion of the title compound. 2,2', 3,3', 6,6'-hexamethyl- 4,4'-biphenol has been isolated as an intermediate. The product is an intermediate in Vitamin E synthesis. The divanadium substituted phosphomolybdates are found to catalyze the oxidation dialkylphenols to diphenoquinones. The rate is highly dependent on the oxidation potential of the substrate and the reaction proceeds by electron transfer from the substrate to the heteropolyanion catalyst [59].

The divanadium substituted heteropolyanion has been found catalyze aerobic oxidation of dialkyl phenols to diphenoquinones and the oxidation of 2,3,5-trimethyl phenol to 2,3,5-trimethyl-1,4-benzoquinone has been accomplished by Lissel *et al*. The rate is found to be dependent on the oxidation potential of the substrate and proceeds by electron transfer from the substrate to the heteropolyanion catalyst [60]. These catalysts are equally efficient for oxybromination in organic medium. Thus oxybromination of phenol, anisole, o-cresol, p-cresol, 1-naphthol, N,N-diethyl aniline, toluene, cumene, acetone, cyclohexanone and 1-octene to the corresponding bromides has been achieved in ambient conditions by Neumann *et al*. The di vanadium substituted complex is dissolved in a non-polar chloro hydrocarbon solvent by complexation with tetraglyme [61].

Nakayama and co-workers were successful with the oxidation of benzylic derivatives with oxygen catalyzed by mixed addenda metallophosphate containing vanadium and molybdenum. Thus $(NH_4)_6$ $[PMo_6V_6O_{40}]$ catalyzed oxidative dehydrogenation of benzylic amines to the corresponding Schiff base amines with oxygen in toluene solution at 100°C. Isochroman and indan are oxidized to 3,4-dihydroisocoumarin and 1-indanone with high selectivity [62].

Oxidative cleavage of ketones such as substituted cycloalkanones, 1- phenylalkanones and open chain ketones to the corresponding acids was observed by El Ali et al. Thus substrates such as 2,4-dimethyl cyclopentanone are oxidized to 5-oxo-3- methyl hexanoic acid and 1- phenylpropan-1-one to a mixture of benzoic and acetic acid. Open chain ketones such as pentan-3-one is oxidized to the corresponding carboxylic acid [63].

The mixed addenda system can act as catalysts in the presence of a co-catalyst. The most common system in operation is the vanadium substituted phosphomolybdate in conjunction with Pd(II) for the oxidation of olefins to carbonyl compounds. This is analogous to Wacker oxidation process based on $CuCl_2$ and Pd(II). In contrast to Wacker process the HPA system works at very low chloride concentration or even in its absence. In addition the HPA is more active, selective and less corrosive. Other examples of such two component catalytic system include Tl^{3+} /Tl^{+}, Pt^{4+} / Pt^{2+},Ru^{4+} / Ru^{3+}, Ir^{4+} / Ir^{3+}, Br_2 / Br^- and I_2 / I^- [15].

Atlamsani and co-workers have successfully carried out the oxidation of 2- methyl cyclo hexanone and cyclohexanone by dioxygen to 6-oxo- heptanoic acid and adipic acid respectively. The catalysts in use were molybdovanadophosphoric acids [64].

1.7.2.2 Oxidation by hydrogen peroxide

Hydrogen peroxide is an important and a widely used oxidant for the organic substrates for the simple fact that it is cheap, easily available and affords water as harmless side product which is environmental friendly. A wide range of oxidation processes such as epoxidation and hydroxylation can be accomplished with Keggin heteropoly compounds.

As the heteropoly compounds are generally insoluble in organic substrates they are rendered soluble by using alkyl ammonium groups as the counter cations. Tungsten and molybdenum compounds are efficient catalysts for oxidation by hydrogen peroxide. Tungsten and molybdenum containing polyoxometalates catalyze the oxidation of a wide range of organic substrates for a large variety of reactions. The reaction proceeds in homogeneous or in a two phase system. Peroxo polyoxometalates have been shown to be the active intermediates in these reactions. Two efficient and mechanistically closely related catalyst systems involving polyoxometalate mediated hydroperoxide oxidation were developed by Ishii and Venturello. Ishii demonstrated that the oxidation of organic substrates with commercially available 35 % H_2O_2 is performed in homogeneous or more often in biphasic system. This system involves catalyst comprising the heteropolyacid, tungstophosphoric or molybdophosphoric acid and cetylpyridinium chloride. The latter provides a phase transfer function. The tri- cetylpyridinium salts of tungstophosphoric acid is prepared by the reaction of the heteropolyacid with three equivalents of cetylpyridinium chloride. According to the reaction mechanism proposed the reaction proceeds in the presence of the heteropolyacid as the catalyst precursor. An active peroxo polyoxometalate species is formed in the aqueous phase by the interaction of the Keggin heteropolyoxometalate with H_2O_2. With the phase transfer agent i.e., the cetylpyridinium cation, this peroxo polyoxometalate is almost fully transferred to the organic phase as it is soluble in the organic solvent. The reaction takes place in the organic phase via oxygen transfer from the peroxo polyoxometalate to the substrate. Peroxo polyoxometalate is then regenerated at the interface by interaction with H_2O_2. Epoxides with good yields and selectivity are obtained with this system [15].

Venturello system involves the epoxidation of alkenes in a biphasic system e.g.water-chloroform at 60-70°C with the use of dilute H_2O_2 as the oxidant with tungsten and phosphate ions as catalyst precursors in the presence of a phase transfer catalyst i.e. quaternary ammonium cation (Q^+) with C_6 – C_{18} alkyl group. The peroxo polyoxometalate $\{PO_4[WO(O_2)_2]_4\}$ is the active oxygen transfer agent which is isolated and characterized. This peroxo polyoxometalate has C_2 symmetry with a central tetrahedron linked through its oxygen atoms to two pairs of edge sharing distorted pentagonal pyramids $W(O_2)_2O_3$. Each tungsten is linked to two peroxo groups one non-bridging and the other bridging located in the equatorial plane of pentagonal bipyramid [15].

Thus epoxidation of 1-octene was achieved in a biphasic system by Aubry *et al* [65].

The oxidation of trimethoxy benzene to dimethoxy-para- benzoquinone in acetic or formic acid medium was achieved at 30°C by Orita *et al*. The catalysts include molybdophosphoric acid, molybdosilicic acid and tungstophosphoric acid [66].

Aromatic amines are oxidized with H_2O_2 catalyzed by cetylpyridinium salts of heteropolyoxometalates by Sakaue *et al*. Thus substituted anilines were oxidized to nitrosobenzenes or nitrobenzene at room temperature under two-phase conditions in chloroform solvent. At room temperature the anilines are converted to nitrosobenzenes while at elevated temperature nitrobenzene is the chief product. Reaction in aqueous medium affords azoxybenzene [67].

Ishii and co-workers have reported the oxidation of sulphides to sulphoxides and sulphones by two phase reaction conditions in chloroform as solvent with 93 –99 % [68].

Oxidation of aliphatic and aromatic amines with hydrogen peroxide is catalyzed by peroxo heteropolyoxometalate by Sakaue *et al*. The primary amines were oxidized under homogeneous conditions in tert-butanol as solvent while the secondary amines were oxidized under heterogeneous conditions in chloroform to oximes and nitrones respectively. The aromatic amines were oxidized to nitroso or nitro compounds [69].

Oxidation of olefins and alcohols by peroxo molybdenum complex derived from triscetylpyridinium 12- molybdophosphate and hydrogen peroxide in chloroform. The complex $Q^{3+}\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ (where $Q^+ = [(C_6H_{13})_4N^+]$) in conjunction with H_2O_2 as the primary oxidant in aqueous / organic biphasic system was developed by Venturello *et al* . Water insoluble inactivated alkenes, internal or terminal, open chain or cyclic, isolated or carrying diversified functionalities were epoxidized in high yields under mild reaction conditions in a short reaction time [70].

Ballistreri and co-workers were successful with the oxidation of alkynes both internal and terminal by hydrogen peroxide in the presence of $(cetylpyridinium)_3$ $(PMo_{12}O_{40})$. The activity of this system was compared with an analogous oxidation catalyzed by Na_2MoO_4 where [M = Mo(VI), W(VI)]. The heteropoly system was found to perform better than the MO_4^{2-} system. Higher catalytic activity of peroxometalate allows the oxidation of internal alkynes by H_2O_2 which does not occur with MO_4^{2-} system [71].

The versatile transformation of vic-diols to hydroxy ketones with H_2O_2 was performed with Sakata *et al* by peroxotungstophosphates at reflux temperatures of chloroform. Thus 1,2 hexanediol and 1,2-ctanediols were converted respectively to 1-hydroxy-2-hexanone and 1-hydroxy- 2- octanone at yields above 90 % [72] .

Tris cetylpyridinium – 12- tungstophosphate provided an alternate method developed by

Oguchi and co-workers to prepare epoxy acids from α, β unsaturated acids. Crotonic acid was chosen as the model substrate [73].

Matoba *et al* have performed the epoxidation of allylic alcohol with H_2O_2 by a new catalytic system prepared from 12- molybdophosphoric acid and cetylpyridinium chloride under two phase conditions in chloroform. Substrate such as geraniol, 3- hydroxy- endo- tricyclo deca- 3,8- diene were taken for study [74].

Shimizu *et al* have carried out the oxidation of 2,6-di-tert- butyl-4-methyl phenol in acetic acid to yield hydroperoxide which converts into para benzoquinone. This reaction has been carried out with a wide range of catalysts such as molybdophosphoric acid, molybdosilicic acid and tungstophosphoric acid and their respective sodium salts [75].

The transition metals incorporated in the Keggin framework are efficient oxygen transfer agents with oxidants such as hydrogen peroxide are found to catalyze oxidation of alkanes, alkenes and aromatic compounds. The activation of the relatively inert C-H bond via oxygen insertion is catalyzed by the transition metal substituted heteropolyanions using H_2O_2. Diiron substituted polyoxometalates were found to be highly efficient for the selective oxygenation of cyclohexane with hydrogen peroxide. Other alkanes such as n-hexane, n- pentane and adamantane were catalytically oxygenated with this system by Mizuno and his fellow workers. The efficiency and activity for the use of hydrogen peroxide greatly depends on the iron centers and the diiron substituted complexes showed the highest efficiency for hydrogen peroxide conversion [76].

The catalytic properties of the transition metal substituted polyoxometalates of the kind $[PM(L)W_{11}O_{39}]$ where M = Fe(III), Cr(III), Ru(IV), Ti(IV) and V(IV) were studied by

Kuznetsova *et al* for substrates such as cyclohexene, benzene, alcohols and aldehydes with hydrogen peroxide and other oxidants [77].

Titanium substituted polyoxotungstate with the composition $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ where x =1,2 and peroxo titanium complexes were found to be efficient catalysts for alkene epoxidation reactions with H_2O_2. Toshihiro *et al* established that the epoxidation results from the synergistic interaction between a tungsten- peroxo site with an adjacent Ti-peroxo (μ) site which acts as electrophilic center for the alkene on the catalyst. The kinetic feature for the epoxidation implies the involvement of .OH radicals with the competition with H_2O_2 dismutation [78].

Catalytic properties of heteropoly complexes containing Fe(III) ions and heteropolyanion $PW_{11}O_{39}^{7-}$, isolated from aqueous solution as tetrabutyl ammonium salts were established by Kuznetsova et al for the oxidation of benzene by hydrogen peroxide in acetonitrile medium at 70°C. Different types of iron containing complexes have been identified. The mechanism of H_2O_2 activation by one of the complexes i.e., $[PW_{11}O_{39}Fe(OH)]^{5-}$ includes most likely the initial formation of a peroxo complex which was observed in the electronic spectra [79]. Chromium containing derivatives of $PW_{11}O_{39}^{7-}$ were synthesized by Kuznetsova and his co-workers and these were used as catalysts for the oxidation of unsaturated hydrocarbons such as benzene and cyclohexene with hydrogen peroxide. The surface location of Cr(III) is supposed to favour oxygen transfer from hydrogen peroxide to hydrocarbon. The resulting oxidized species $PW_{11}Cr[O]$ are active oxidants in the reaction with unsaturated hydrocarbons [80].

Keggin type polyoxotungstates as catalysts in the oxidation of cyclohexane by dilute hydrogen peroxide were utilized by Simoes *et al.* The reactions were carried out in acetonitrile medium, using tetrabutyl ammonium salts of the complexes. The polyanions $PW_{11}O_{39}^{7-}$ and $[PW_{11}Fe(H_2O)O_{39}]^{4-}$ shows higher catalytic activity and different selectivity for oxidation than the corresponding Cu, Co, Mn and Ni substituted complexes [81]. Oxygenation of alkenes such as cyclooctene, 2-octene, 1-octene, cyclohexene, styrene and trans- stilbene was found to be effected by catalytic amounts of di-iron substituted silicotungstate with high and efficient utilization of H_2O_2. Mizuno and his team of workers showed that this type of catalysts accounted for the highest efficiency of H_2O_2 utilization and conversion. The structure of iron centers remarkably influenced the catalytic activities, the di-iron substituted silicotungstate being specifically the most active for the oxidation of cyclohexane, cyclohexene and trans-stilbene [82].

Mizuno et al found the catalytic activities of di-iron substituted silicotungstate to be 101-102 times higher than those of non, mono, and tri-iron substituted silicotungstates [83].

Characteristic features of vanadium containing heteropoly catalysts for the selective oxidation of hydrocarbons has been described by Misono *et al*. Conversion on the basis of H_2O_2 was 93 % for oxidation of benzene to phenol with 100 % selectivity on the basis of benzene [84].

Using selectively site substituted vanadium (V) Keggin heteropolytungstates the catalytic activities for the hydroxylation of benzene in the presence of aqueous hydrogen peroxide was examined by Nomiya and fellow workers under atmospheric pressure in a two liquid phase, aqueous and organic. The activities and stabilities of catalysts were compared with those of vanadium(V) – substituted Dawson HPA's vanadium(V) – containing isopolyanions, the Milas reagent and the picolinato- vanadium (V) oxo peroxo complex [85].

Functional action of Keggin- type mono- vanadium (V) – substituted heteropolymolybdate as a single species on benzene hydroxylation in the presence of hydrogen peroxide was investigated by Nomiya and his team. The experimental observations suggested that the catalysis by $PMo_{11}V$ is due to the cooperative interaction of the molybdenum framework with one vanadium(V) center. The marked stability of these catalysts precursors was established in benzene hydroxylation [86].

Neumann et al have shown that Keggin type mixed addenda heteropolyanions containing vanadium atom such as $PMo_{10}V_2O_{40}^{5-}$ are effective as catalysts for the oxidation of alkyl aromatics to respective acetates or alcohols and aldehydes or ketones using 30 % H_2O_2 as oxidant in acetic acid. The catalyst is not degraded during the catalytic cycle. The reaction proceeds by homolytic cleavage of $PMo_{10}V_2O_{40}^{5-}$ - peroxo intermediate. The resulting hydroperoxy and hydroxy radicals initiate the formation of benzyl radicals which lead to product formation [87].

1.7.2.3 Oxidation with tertiary butyl hydroperoxide and others.

Other oxidants such as tertiary butyl hydroperoxide (TBHP), iodosyl benzene (PhIO), sodium periodate($NaIO_4$), potassium per sulphate ($KHSO_5$), meta perchloro benzoic acid (MPCBA) etc. are successfully operatable with transition metal substituted polyoxometalates and mixed addenda heteropolyacids. Oxidation of para substituted phenols using TBHP- heteropolyacids system was accomplished by Shimizu and his team of scientists in acetic acid medium at 35°C. Thus 4- tert- butylperoxy –2,5-cyclohexadien-1-one was obtained in good yields by the oxidation of 2,4,6-trialkyl substituted phenols using $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_4SiMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$ as the catalysts [88].

Transition metal substituted polyoxometalates and mixed addenda heteropoly compounds are good oxygen transfer agents with the above oxygen donors and are efficient for the oxygenation of a wide variety of hydrocarbons. Extensive catalytic work has been reported with ruthenium substituted heteropoly compounds with a variety of oxidants. Bressan and the team of workers used $K_5[Ru(H_2O)PW_{11}O_{39}]$ as catalyst for the oxidation of a series of saturated hydrocarbons such as adamantane, cyclooctane, cyclohexane, hexane and heptane with TBHP and hypochlorite as the source of oxygen. Hypochlorite oxygenation proceeds via oxo-metal species [89].

Neumann *et al* have reported the successful utilization of ruthenium substituted heteropolycomplexes of the type $[Q_4N]_5[SiRu(L)W_{11}O_{39}]$ where Q is (C_6H_{13}) with oxidants TBHP, $KHSO_5$, PhIO, $NaIO_4$ for the oxidation of alkanes and alkenes. Thus liquid phase oxidation of alkanes such as adamantane, cyclohexane and alkenes such as oct-1-ene, styrene proceeded with high activity and selectivity. The activity and selectivity varied with the oxidant used. With periodates selective bond cleavage proceeded to give aldehydes as the exclusive product. The oxidation of styrene with per iodates gave benzaldehyde as the chief product. Investigation of reaction kinetics, substituent effect and isotope incorporation enabled the formulation of reaction mechanism. Interaction of styrene with the catalyst forming a metallocyclooxetane which rearranges in the rate determining step to a cyclic diester through two different transition states depending on the substituent. In the final step the cyclic diester decomposes yielding the cleavage product [90, 91].

Rong and co-workers epoxidized trans- stilbene by iodosyl benzene with a series of complexes of the kind $[PW_{11}O_{39}Ru^{II}(L)]$ where L = Me_2SO, $(CH_2)_4SO$, Ph_2SO,

Me_2S,methyl cysteine, maleic acid, fumaric acid, crotonic acid, 1,4- dihydroxybut-2-ene and pyridine [92].

Faraj and his team found that other transition metal substituted heteropolytungstates proved to be effective for the oxidation of hydrocarbons on interaction with alkyl hydroperoxides. The product yields and stabilities of these systems are higher than those of other homogeneous catalytic alkane oxygenation systems reported in literature. Thus tetra n- hexylammonium salts of transition metal substituted heteropoly complex of the kind $[PW_{11}(M)O_{39}]$ with M = Co^{II}, Mn^{II}, Fe^{II} catalyzes the oxidation of organic substrates such as cyclo-C_6H_{12}, C_6H_5But and $Me_2CHCHMe_2$ in different solvents [93].

Divanadium containing phosphomolybdates with TBHP were found to oxidize thioether mustard analogs at 25°C by Gall et al. The reaction tends to proceed by initial thioether oxidation and polyoxometalate reduction followed by reduced polyoxometalate reoxidation by TBHP. This is in sharp contrast to the conventional mechanism for metal complex mediated peroxide oxides (electrophilic peroxide activation by metal complex or radical process) [94].

1.8 General Applications

The wide range of applications of heteropoly compounds are based on their unique properties which include size, mass, electron and proton transfer (storage abilities), thermal stability, lability of “lattice oxygen”and high Bronsted acidity of the corresponding acids. An added advantage is that the heteropolyacids can be separated and enriched and can be extracted into organic solvents. There are more commercial applications of polyoxometalates than other class of cluster compounds and promise for additional application in areas from catalysis and medicine to materials and micro device technology is substantial. Polyoxometalates have long been used for detection, separation and quantitation based on properties like their high molecular weight, their electrochemical activity and reducibility to form coloured species and the fact that a wide variety of elements can be incorporated in the polyanion framework.

Analysis

Among the earliest and the most widely used application has been the determination of phosphorus and silicon either by gravimetric and physical methods after reduction to heteropoly blues. Similar applications include the determination of P, Si, Ge and As by differential pulse voltammetry, chromatographic (HPLC) separations and measurements of nanomolar concentrations of silica in sea water. Analytical determination of elements such as Ti, Zr, Hf, Th, Nb, Ce and Sb are based upon structurally undefined complexes of these elements with $[PMo_{12}O_{40}]^{3-}$ or $[SiMo_{12}O_{40}]^{4}$.

Biochemical Applications

Many pharmaceutical and biological samples are routinely determined by using poly- oxometalates.

Ability of the polyoxometalate to coagulate proteins and to precipitate organic molecules like alkaloids is important in this connection. The acid $H_3PW_{12}O_{40}$ either in aqueous or ethanolic solution is used as non-specific electron- dense stain for electron microscopoy. These staining and precipitant applications are based on coulombic interaction between

polyanion and the cationic sites on the biomolecules. Polyoxometalates find their use in clinical chemistry and in other biologically active molecules. The dyestuffs industry has for many years utilized heteropolymolybdates and tungstates to form colour lakes or toners from basic dyes. The electron acceptor properties in $[SiMo_{12}O_{40}]^{4-}$ and $[SiW_{12}O_{40}]^{4-}$ are made use of in photosynthesis and photophosphorylation studies. Large heteropolytungstate anion like $[SiW_{12}O_{40}]^{4-}$ and $[BW_{12}O_{40}]^{4-}$ exhibit antiviral and antitumoral properties at non- cytotoxic doses *in vitro* and *in vivo* and are potent inhibitors of cellular, bacterial and viral DNA and polymerases.

Catalysis

Heteropolyacids are used as heterogeneous catalysts for a wide variety of reactions like oxidation of propylene and isobutylene to acrylic and methacrylic acids, and ammoxidation of acrylonitrile, oxidation of aromatic hydrocarbons, olefin polymerization and epoxidation and hydro desulphurization.

Solid heteropolyacids are known to be efficient as catalysts for polycondensation of benzyl alcohols, and Friedel – Crafts type alkylation, acylation and sulphonation of aromatics, for oxidation of butadiene to furan and for dehydration of alcohols.

Heteropolyanions in homogeneous solution have received recent attention. Mixed addenda system coupled with Pd (II) salts are known to effectively catalyze aerial oxidation of olefins. Following are some of the industrial processes in operation wherein heteropoly compounds are used as catalysts (a) oxidation of methacrolein (b) hydration of olefins (propene and butene) (c) polymerization of tetrahydrofuran (d) methyl tertiary butyl ether synthesis.

Other applications

Insoluble salts of heteropolyanions such as the ammonium molybdophosphate are long in use and are available as ion-exchange materials. Reduced hetropolyacids are used to detect alcohol or carboxylic acid radicals generated by radiolysis of aqueous solutions. Heteropoly complexes are used as flame retardants and smoke suppressants or as corrosion inhibitors and conversion coatings on steel and aluminium are reported. Crystalline 12-tungstophosphoric and 12- molybdophosphoric acid are good protonic conductors and both these acids are electrochromic in the solid state as a consequence of formation of the reduced species [1, 95].

1.9 Characterization techniques for Keggin heteropoly compounds

1. Chemical analysis

This method includes techniques like elemental micro analysis, atomic absorption spectroscopy and X-ray flourescence .

2. Infrared spectroscopy

Vibrational spectroscopy is an extensively used tool in polyoxometalate chemistry mainly for structure elucidation. The stretching frequencies in the Keggin type heteropoly compound depends on the nature of the metal-oxygen linkages found in the complex. There are four types of metal-oxygen linkages present in the Keggin structure ($XM_{12}O_{40}$) : four O_i (internal oxygens connecting X and M), twelve O_e (edge-sharing oxygen connecting M's), twelve O_c

(corner- sharing oxygen connecting M_3O_{13} units) and twelve O_t (terminal oxygen bonding to one M atom). The metal atoms are displaced outward from the center of the octahedron, giving the M-O_t bond a double-bond character. The internal oxygen is located inside the anion and the M-O_iX bond is long and weak. The region of interest for Keggin type heteropoly compounds is from 1100- 600 cm^{-1} where the absorptions due to metal-oxygen stretching vibrations occur. In table-4 the characteristic IR bands with assignments given by Rocchicciolini – Deltcheff et al. are summarized [96].

Table-4

IR Bands characteristic of Keggin Anion, α-$XM_{12}O_{40}$ (cm^{-1})

	PW_{12}	PMo_{12}	SiW_{12}	$SiMo_{12}$
(X-O)	1080-1081	1062- 1068	920-928	899-904
($M-O_t$)[a]	976-995	954-975	967-981	940-957
($M-O_cM$)	890-900	869-880	878-894[b]	855- 868
(M-Oe-M)	805-810	785-810[b]	780-797	770-795

a shoulder peaks which sometimes appear at about 10 cm^{-1} higher than the main peak are included in the range of wave number.

b in some cases , α- SiW_{12} and α- PMo_{12} show a doublet.

The Si-O, Ge-O and P-O stretching vibrations at 923, 830 and 1080 cm^{-1} respectively shows higher frequencies than the simple XO_4^{n-} anions suggesting higher π- bond character of the X-O bond present in the Keggin unit.

Stretching frequencies in lacunary heteropolyanions

The stretching frequencies in lacunary heteropolyanions are of a different nature compared to those observed in the Keggin structure [2].

Keggin related compounds α- $XM_{11}O_{39}^{n-}$ have a defect structure in which one metal atom and its terminal oxygen atoms are missing. These anions have a hole surrounded by five oxygen atoms and they behave as pentadentate ligands. A general splitting of P-O stretching frequencies is interpreted as a weakening of anion cohesion. In particular, the decrease in frequency of asymmetric bridge stretching is consistent with the lowering of $M-O_c-M$ angles. The P-O stretching band for $PW_{11}O_{39}^{7-}$ is split into 1085 and 1040 cm^{-1}.

This splitting is due to change of symmetry from T_d (XM_{12}) to C_s(XM_{11}) leads to the broadening of the band and there by causes splitting in the frequency. Table-5 gives the characteristic frequencies of the lacunary anion.

Table-5

I.R bands for lacunary heteropolyanions

(potassium and ammonium salts)

$PW_{11}O_{39}^{7-}$	$PMo_{11}O_{39}^{7-}$	$SiW_{11}O_{39}^{8-}$	$SiMo_{11}O_{39}^{8-}$	Nature of bond
1085 1040	1060			ν_{av}(P-O)
	1010			
950	930 900	952	930 910	ν_{av}(M-O_d)
		885	870	ν_{av}(Si-O)
900 860 810 725	860	870	830	ν_{av}(M-O_b-M)
	790 742	797 725	740	ν_{av}(M-O_c-M)

3. UV- Visible spectroscopy

The electronic spectra of the Keggin type heteropoly compounds find use in structural and quantitative analysis. These compounds with Keggin structure absorb mainly between the region 180- 270 nm. The electronic absorption spectra give information about the electronic state of the compound [3]. The incorporation of a transition metal in the framework shows intensive bands in the visible region. The position of the band depends on the nature of the transition metal incorporated in the lacunary vacancy. The electronic absorption spectroscopy can be used as a technique for postulating a reaction mechanism especially for oxidation reactions by performing *in situ* study of the reaction mixture. The changes observed in the spectra can be correlated to the formation of the active intermediate formed due to the interaction between the active center in the catalyst and the oxidant. These changes are usually observed as appearance of a new band or increase in the absorption intensity with time.

4. Nuclear Magnetic Resonance spectroscopy

NMR spectroscopy is a valuable tool to study the electron density distribution due to large chemical shifts induced both by paramagnetic atoms and electron transfer between atoms in diamagnetic HPA. The NMR chemical shift with diamagnetic system in solution arises from two contributions, diamagnetic and paramagnetic. The diamagnetic term is determined by the potential created by the inner electrons. The paramagnetic contribution determines the variation of the observed chemical shift. The structural details of the Keggin type heteropoly comlpexes can be elucidated by this type of spectroscopy. Several important elements can be measured easily. The most widely investigated nuclei include ^{31}P, ^{183}W , ^{51}V, ^{1}H and ^{17}O. When their catalytic, electrochromic and other properties are used, they participate in redox reactions with rather specific electron density transfer. Studies of the electron density distribution both in the diamagnetic and paramagnetic species are quite important for understanding the nature of chemical bonding in HPA and their role in chemical reactions.^{17}O NMR spectroscopy gives information about the bonding nature of the oxygen atoms. There is a correlation between the downfield shift and the decreasing number of metal atoms to which the oxygen atom is bonded. ^{17}O NMR spectroscopy is not fully utilized due to the low natural abundance of ^{17}O.^{1}H NMR is an important and widely used tool for the detection of the different types of protons present in the heteropoly compound. There is observed a change in the type of spectrum with the number of water of hydration. The ^{31}P chemical shifts provides information about structure, composition and the electronic state of these materials. The chemical shifts in the aqueous solution is correlated with X-O bond strength. The ^{31}P NMR chemical shifts is greatly dependent on the degree of hydration in 12-phosphotungstic acid, values being -15.1 to -15.6 ppm for n =6 and -11.1 to -10.5 ppm for n =0. The difference is explained as follows, in the former protonated water, $H(H_2O)_2+$, is connected with the heteropolyanion by hydrogen bonding at terminal oxygen and in the latter the protons are directly attached to the oxygen atoms of the polyanion. ^{31}P NMR is an important and widely used tool for structure description especially in mixed addenda heteropoly compounds due to the presence of number of structural isomers which increases with the number of addenda atoms. ^{51}V NMR is widely investigated for the structural elucidation in vanadium containing mixed addenda heteropoly compounds due to the large natural abundance of ^{51} V nuclei. The number of structural isomers increase with the increase in the number of addenda atoms and their position in the Keggin structure is confirmed by ^{51}V NMR spectroscopy [97].

5. Electron spin resonance spectroscpoy (ESR spectroscopy)

This spectroscopy is well suited to study delocalization problems and spin density distribution but is limited to systems with unpaired electrons. ESR spectroscopy gives information about site symmetry and electronic structure of a paramagnetic metal ion in an polyanion. ESR spectra gives information about mixed valence structure of reduced heteropoly compounds. The presence of unpaired spin in reduced HPA species gives rise to an EPR spectrum whose pattern depends considerably on the number of atoms aquiring the unpaired electrons and temperature. For axial MO_6 complexes to which the reduced form of HPA containing V^{4+}, Mo^{5+} or W^{5+} belong, the EPR spectrum has an anisotropic pattern at low temperature and may be described by the spin Hamiltonian

$$\kappa = g_{\parallel}\beta H_z S_z + g_{\perp}\beta\,(H_x S_x + H_y S_y) + A_{\parallel} S_z I_z + A_{\perp}(S_x I_x + S_y I_y)$$

where S = electronic spin

I = nuclear spin

A = hyperfine splitting constant

At elevated temperature the EPR spectrum becomes isotropic due to molecular tumbling and electron delocalization over several atoms. Presence of a non-degenerate d_{xy} orbital for each octahedron allows these HPA's to be reversibly reduced with one or more electrons with retention of the original structure. Reduction of the anion results in the blue colour due to intervalence band. The one electron reduced species gives EPR spectra which have been interpreted to show complete delocalization of the unpaired spin over the twelve metallic atoms. The EPR spectra at different temperatures have shown that one electron is trapped at quite low temperatures with only a partial delocalization but is completely delocalized at higher temperatures. This suggests that the spin is partially localized in the ground state but is involved in rapid thermal hopping from one site to another at elevated temperatures. This unpaired electron resides on a more easily reduced metallic atom. The degree of electron delocalization in the ground state is determined by the extent of interaction in the bridges [97].

5. Electrochemistry of Keggin heteropoly compounds

Heteropoly compounds can act as redox active materials by changing the heteroatom, the transition metal, without affecting the basic Keggin structure. The vast chemistry of heteropolyanion involves oxidation / reduction of addenda or the active transition metal. The electrochemical analysis of such species forms the basis of identification of redox active species. Thus electrochemical technique such as cyclic voltammetry is a means to understand the reactivity and mechanistic behaviour of heteropolyanions as redox agents and redox catalysts. The wide range of counter cations helps in studying the redox behaviour of these anions in a variety of solvents from water to a large number of organic solvents. The heteropolyanions undergo rapid one and two electron reversible reduction to produce the heteropolyblues and further irreversible reduction can lead to their concomitant decomposition. Reduction is accompanied by increase in the charge density and basicity. Reduction can also be accompanied by protonation depending on the pK_a of the produced oxometalate. The reduction potentials of the Keggin type heteropoly tungstates and heteropoly molybdates are controlled by factors such as the nature of isomers. The reducibility increases in the sequence α, β, Υ isomers. The reduction potential of one electron waves is found to decrease linearly with a decrease in the valence of the central metal or an increase in the negative charge of the heteropolyanion. The transition metal incorporated in an heteropolyanion resides in an octahedral environment with one coordination site occupied by a solvent molecule, mostly water. This is oxidisable to corresponding oxometal, hydroxometal or peroxometal derivative depending on the nature of the metal and the oxidant. These species play an important role in oxidation catalysis and hence in synthetic application. The formal redox potential depends on a number of factors such as nature of the heteroatom and the addenda atom. The redox potential of the metal increases with increasing formal charge on the central atom. For a given oxidation state, the redox potential increases with the size and decreasing electronegativity of the central metal atom. The electrolytic conditions such as pH, counter cation and the nature of the solvent also play an important role in deciding the formal redox potential. By varying the addenda atom the electrochemical character of the polyoxometalates can be changed. The addenda atoms can be arranged in decreasing oxidising ability in the following order

V (V) > Mo (VI) > W (VI).In case of one electron reduced mixed addenda heteropolyanions the added electron is localised on the more reducible atom at room temperature [98].

7. Thermal Analysis

The TG, DTA and DTG measurements gives an idea about the number and nature of water molecules present in the HPA. The results of thermogravimetric analysis shows the presence of two types of water in heteropoly compounds, i.e., “water of crystallization” and “constitutional water molecules”. The loss of former usually occurs at temperatures below 473 K. At temperatures exceeding 543 K for $H_3PMo_{12}O_{40}$ or 623 K for $H_3PW_{12}O_{40}$ the constitutional water molecules (the acidic protons bound to the oxygens of the polyanion) are lost. The DTA, TG and DTG of molybdovanadophosphoric acids of the series $H_{(3+x)}Mo_{12-x}V_xO_{40}$. n H_2O with the highest content of water of crystallization (n = 19-34) melts above 40°C, giving solutions of heteropolyacids which boil at 110°C to 130°C. The total loss of crystallization of water occurs below 170-200°C [99].

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CHAPTER –2

EXPERIMENTAL

2.0 EXPERIMENTAL

2.1 Synthesis of heteropolycompounds

Synthesis of $K_5[PW_{11}TiO_{40}]. nH_2O$

Synthesis of $K_7[PW_{10}Ti_2O_{40}]. nH_2O$

Synthesis of $K_2[Bu_4N]_5[PW_{10}Ti_2O_{40}]. nH_2O$

2.3.7 Cyclic Voltammetry

2 EXPERIMENTAL

2.1 Synthesis of heteropolycompounds

Synthesis of $K_5 [PW_{11}TiO_{40}] .nH_2O$

Solution of lithium acetate dihydrate (10 gm, 98.01 mmol) made in 30 ml water was brought to pH 6 with acetic acid. A solution of phosphotungstic acid (10 gm, 3.25 mmol) in water (35 ml) was added to form $PW_{11}O_{39}^{7-}$ in situ. Then one ml quantity of $TiCl_4$ was added dropwise with stirring. After the addition, the mixture was refluxed for 20 minutes, cooled to room temperature and filtered through an analytical filter aid. The precipitated solid was recrystallised from water.

Synthesis of $K_7[PW_{10}Ti_2O_{40}]$. nH2O

Sodium dihydrogen phosphate dihydrate (3 gm, 19.23 mmol) was added to a solution of solution of sodium tungstate dihydrate (15 gm, 45.47 mmol) in 50 ml water. Titanium tetrachloride (0.9 ml) was added dropwise with stirring. The mixture was refluxed for a period of 20 minutes followed by filtration through an analytical filter aid. The clear, colourless filtrate whose pH was 8.2 was cooled. To this was added solid potassium chloride (7.5 gm). The white product obtained was separated by filtration and recrystallized from water and used for catalytic study.

Synthesis of $K_2[Bu_4N]_5[PW_{10}Ti_2O_{40}]$. nH_2O

Excess solid tetrabutyl ammonium bromide is added to the aqueous solution of $K_7[PW_{10}Ti_2O_{40}]$. The white coloured product obtained was recrystallized from water.

Synthesis of $Na_{2.25} [(CH_3)_2(C_6H_5)(C_6H_5CH_2)N]_{4.75} [PW_{10}Ti_2O_{40}].nH_2O$

Sodium dihydrogen phosphate dihydrate (6 gm, 43 mmol) was added to a solution of sodium tungstate dihydrate (30 gm, 91 mmol) in 100 ml water.

To this was added 1.8 ml of titanium tetrachloride dropwise with constant stirring. The mixture was refluxed for a period of 20 minutes followed by filtration. The pH of the clear and colourless filtrate was checked to be 8.2. Then solid dimethyl phenyl benzyl ammonium chloride (4 gm) was added to obtain a blue precipitate which was separated by filtration and dried.

Synthesis of K_7 $[PW_{10}Ti_2O_{40}]$ supported on silica (10 % w/w)

The catalyst K_7 $[PW_{10}Ti_2O_{40}]$ (0.5 gm) was dissolved in 5 ml water. Coarse silica gel (4.5 gm) was added with constant stirring. The supported catalyst was obtained by evaporating the resultant slurry on a water bath, followed by drying overnight in an oven maintained at 110°C. The dried catalyst was then activated in a furnace at 300°C for four hours.

Synthesis of K_5 $[PW_{11}Co(H_2O)O_{39}]$.n H_2O

Commercially available12-phosphotungstic acid (11.2 g) was dissolved in 25 ml water containing 3 ml glacial acetic acid . The *p*H of the solution was adjusted between 5 and 5.5 with potassium bicarbonate. The solution was boiled and cobalt acetate tetrahydrate (0.8 g) in minimum quantity of water was added with stirring, followed by the addition of potassium acetate (15 g in 8 ml water and 0.5 ml glacial acetic acid). The hot solution was filtered and kept in refrigerator overnight. The purple solid that separated was filtered and air dried.

Synthesis of K_5 $[PW_{11}Mn(H_2O)O_{39}]$.n H_2O

Hydrated 12-phosphotungstic acid (11.2 g) was dissolved in 25 ml water containing 3 ml glacial acetic acid . The *p*H of the solution was adjusted between 5 and 5.5 with potassium bicarbonate. The solution was boiled and manganese acetate tetrahydrate (0.8 g) in minimum quantity of water was added with stirring, followed by the addition of potassium acetate (15 g in 8 ml water and 0.5 ml glacial acetic acid). The hot solution was filtered and kept in refrigerator overnight. Yellow solid that separated was filtered and air dried.

Synthesis of $K_5 [PW_{11}Cu(H_2O)O_{39}].n\ H_2O$

Hydrated 12-phosphotungstic acid (11.2 g) was dissolved in 25 ml water containing 3 ml glacial acetic acid . The *p*H of the solution was adjusted between 5 and 5.5 with potassium bicarbonate. The solution was boiled and copper acetate tetrahydrate (0.8 g) in minimum quantity of water was added with stirring, followed by the addition of potassium acetate (15 g in 8 ml water and 0.5 ml glacial acetic acid). The hot solution was filtered and kept in refrigerator overnight. Green crystals that separated were filtered and air dried.

Synthesis of $K_6 [SiW_{11}Co(H_2O)O_{39}].n\ H_2O$

Hydrated 12-silicotungstic acid (11.5g) was dissolved in 25 ml water containing 3 ml glacial acetic acid . The *p*H of the solution was adjusted to 6 with potassium bicarbonate. The solution was boiled and cobalt acetate tetrahydrate (0.8 g) in minimum quantity of water was added with stirring, followed by the addition of potassium acetate (15 g in 8 ml water and 0.5 ml glacial acetic acid). The hot solution was filtered and kept in refrigerator overnight. Deep red crystals that separated were filtered and air dried.

Synthesis of $K_6 [SiW_{11}Mn(H_2O)O_{39}].n\ H_2O$

Commercially available hydrated 12- silicotungstic acid (11.5 gm) was dissolved in 25 ml water containing 3 ml glacial acetic acid. The pH of the solution was adjusted to 6 with potassium acetate. The resulting solution was boiled and then manganese acetate tetrahydrate (0.8 gm, 3.21 mmol) dissolved in minimum quantity of water was added slowly with stirring.

This was then followed by the addition of a solution of potassium acetate (15 gm dissolved in 8 ml water containing 0.5 ml acetic acid). The hot solution was then filtered and kept in refrigerator overnight at 4°C. The yellow solid that formed was separated by filtration and then air dried.

Synthesis of K_6 $[SiW_{11}Cu(H_2O)O_{39}].n$ H_2O

Pure and hydrated 12-silicotungstic acid (11.5g) was dissolved in 25 ml water containing 3 ml glacial acetic acid . The *p*H of the solution was adjusted to 6 with potassium bicarbonate. The solution was boiled and copper acetate tetrahydrate (0.8 g) in minimum quantity of water was added with stirring, followed by the addition of potassium acetate (15 g in 8 ml water and 0.5 ml glacial acetic acid). The hot solution was filtered and kept in refrigerator overnight. The whitish blue solid that separated was filtered and air dried.

Synthesis of H_4 $[PMo_{11}VO_{40}]$. nH2O

Sodium phosphate dibasic dodecahydrate (1.77 gm, 5 mmol), was dissolved in 25 ml water and mixed with sodium metavanadate (1.52 gm, 12.5 mmol) made soluble in 25 ml boiling water. The mixture was cooled and acidified to red colour with 1.25 ml concentrated sulphuric acid. To this coloured solution was added sodium molybdate dihydrate (33.25 gm, 137.42 mmol) in 50 ml of water. Finally 21.25 ml of concentrated sulphuric acid was added. Colour of the solution turned to light red. After cooling the solution was extracted with four fractions each of 25 ml diethyl ether to isolate the heteropolyacid in a separating funnel. In this extraction the heteropoly etherate was present as the middle layer. After separation, a stream of air was passed through the heteropoly etherate layer to free it of ether. The orange solid that separated was dissolved in water, concentrated to the first appearance of crystal in a vacuum desiccator over concentrated sulphuric acid and then allowed to crystallize further. The orange crystals that formed were dried, crushed and used for further studies.

Synthesis of H_5 $[PMo_{10}V_2O_{40}]$. nH_2O

Sodium metavanadate (4.06gm, 33.29 mmol) was dissolved by boiling in 16.6 ml water and then mixed with a solution of sodium phosphate dibasic dodecahydrate (1.18 gm, 3.29 mmol) in 16.6 ml water. To the cooled solution was added 0.83 ml of concentrated sulphuric acid. The resulting solution developed a red colour. Addition of sodium molybdate dihydrate

(20.16 gm, 83.32 mmol) in 50 ml water was then done. While the solution was strirred vigorously 14.16 ml of concentrated sulphuric acid was added slowly and then the hot solution was cooled to room temperature. The title compound was then extracted with four fractions each of 20 ml diethyl ether in a separating funnel. The heteropolyacid was present as the etherate in the bottom layer. This layer was isolated and dried in order to make it ether free. Orange coloured solid was obtained after complete drying. Pure complex was obtained after recrystallization in water. The crystals that formed were dried and crushed for further use.

Synthesis of H_6 $[PMo_9V_3O_{40}]$. nH_2O

Sodium phosphate dibasic dodecahydrate (1.77 gm, 4.95 gm) was dissolved in 12 ml water. Sodium metavanadate (9.15 gm, 75.04 mmol) was made soluble by boiling in 50 ml water. The sodium phosphate solution was mixed with the sodium metavanadate solution. The resulting solution was cooled followed by the addition of 1.25 ml of concentrated sulphuric acid. This red coloured solution was then added to a solution of sodium molybdate dihydrate (13.62 gm, 56.3 mmol) in 37.5 ml water. This solution was stirred vigorously and simultaneously 21.25 ml of concentrated sulphuric acid was added. The hot solution was cooled to ambient conditions. The heteropolyacid formed was extracted with four fractions, each of 25 ml diethyl ether in a separating funnel. The hetropolyacid is present as the etherate in the middle fraction. The middle layer was then isolated, dried to free of ether. The resulting red coloured solid obtained was dissolved in water, concentrated to first crystal formation and allowed to crystallize further. The red crystals that formed were dried and powdered prior to further use.

Synthesis of $[Bu_4N]_4$ $[PMo_{11}VO_{40}]$.n H_2O

Commercially available 12- molybdophosphoric acid (5.9 gm, 2.86 mmol) was made soluble in 25 ml water. Solid lithium carbonate was added in small portions till the pH of the above solution reached 4.3. To this was added sodium metavanadate (0.32 gm, 2.66 mmol) dissolved in 25 ml hot water. The solution was cooled and the pH adjusted to 0.5 with 6M HCl. This solution was stirred in a round bottom flask on a magnetic stirrer for 48 hours at room temperature after which solid tetrabutyl ammonium bromide (4.83 gm, 30 mmol) was added. The immediately produced yellow powder was then stirred with additional 50 ml water for five hours, filtered off, washed thoroughly with 250 ml water, then twice with 50 ml ethanol and finally with 100 ml of diethyl ether (in two fractions of 50 ml). The yellow coloured powder obtained was dried in vacuo prior to further use.

Synthesis of $[NH_4]_4$ $[PMo_{11}VO_{40}]$.n H_2O

Solid ammonium chloride was added in excess to aqueous solution of H_4 $[PMo_{11}VO_{40}]$ to obtain a yellow coloured precipitate which was filtered and dried prior to use.

2.2 Procedure: Catalytic reactions

2.2.1 Catalytic runs

Autoclave reactions

The liquid phase oxidation reactions of substrates such as styrene, cyclohexene and para xylene were carried out under pressure in a stainless steel 300 ml capacity Parr autoclave.

Styrene oxidation was carried out by adding styrene (5.2 gm, 5 mmol), isobutyraldehyde (14.42 mmol), acetonitrile (solvent, 15 ml) and catalyst (65 µmol) to the autoclave. The contents were pressurized with dry air to 440 psi. The temperature in the autoclave was maintained at 60°C under stirring for five hours. The products were analysed by gas chromatograph. Cyclohexene (4.1 gm, 5 mmol) was oxidised under similar conditions as styrene. The liquid products of cyclohexene oxidation were analysed by gas chromatograph and gas chromatograph mass spectrometer.

The liquid phase oxidation of p-xylene was carried out in a stainless steel 300 ml capacity Parr autoclave. The reactants, *p*-xylene (15 g, 140 mmol), water (15 g) tert-butyl hydroperoxide as the initiator (0.3 g) and the catalyst (0.096 mmol) were taken in the autoclave. The reactor was pressurised with air upto 400 psi and kept at 180 with stirring (600 rpm). After an induction period of 2 h, a sudden drop in pressure was observed suggesting the commencement of the oxidation reaction; heating and stirring were maintained till there was no further pressure drop. The autoclave was then cooled to 0^o and gaseous products were released through a gas holder, collected and analysed. The reactor was further repressurised with air upto 400 psi and the reaction was continued at 180^o. This operation was repeated once more. The solid product (6.5 g) was separated by filtration. A sample of the solid product was analysed by esterification by the following procedure: the solid product (0.1g) was dissolved in methanol (5 ml) and BF_3.MeOH (14% solution, 2 ml) was added and the mixture was then refluxed for 6 h. After cooling the sample, water was added and the esters formed were extracted with dichloromethane and analysed by GC. The filtrate portion of the oxidation product consisted of two layers: one was the aqueous layer while the second was organic. Both the layers were separated and analysed. The aqueous layer was extracted with dichloromethane before the GC analysis.

Reactions under atmospheric pressure

The liquid phase oxidation reaction of substrates like benzene, cyclohexane, methyl cyclohexane, naphthalene, methyl naphthalene, biphenyl and phenol were carried out under atmospheric pressure.

The hydroxylation of benzene was carried out in a two-necked 50 ml round bottom flask fitted with a water condenser and a glass stopper and placed in an oil bath maintained at 65°C. In a typical experiment, benzene (1.56 g ,20 mmol), aqueous hydrogen peroxide (2.36 gm, 20mmol), catalyst (0.05 gm ,0.025 mmol) were mixed in 6 mL of acetonitrile and placed in the flask and contents were stirred with a magnetic stirrer. The reaction mixtures withdrawn at regular interval of 30 minutes were analysed by gas chromatography (Hewlett Packard gas chromatograph model No. 5890 Series-II) using HP-5 fused column with 30m x 0.53m x 1.0 μm film thickness and FID detector. Phenol formed in the reaction was confirmed by comparing the retention time with authentic standard and also by GCMS. From the moles of benzene reacted, turnover numbers were calculated. The samples were also analysed simultaneously by UV- Visible and EPR spectroscopy to identify the active intermediate species.

In case of cyclohexane oxidation the reaction was carried out in a two necked 50 ml capacity round bottom flask fitted with a water condenser and a glass stopper and immersed in an oil bath whose temperature was kept constant at 65°C. Thus the reaction mixture contained cyclohexane (1.68 gm ,20 mmol), aqueous hydrogen peroxide (2.36 gm ,20 mmol), catalyst (0.05 gm, 0.025 mmol) and 20 ml acetonitrile. The oil bath was kept on a magnetic stirrer to stir the reaction mixture. The reaction products were analysed by gas chromatograph. The reaction mixture was subjected to ^{51}V and ^{13}C NMR spectroscopy at regular time intervals of half an hour.

In separate experiments methyl cyclohexane (1.96 gm, 10 mmol), naphthalene(1.28 gm, 10 mmol), methyl naphthalene(1.42 gm, 10 mmol), biphenyl (1.54 gm, 10 mmol) were dissolved in 20 gm, 5 gm, 8 gm and 5 gm of acetonitrile respectively, mixed with aqueous hydrogen peroxide (1.18

gm,10 mmol) and catalyst (0.025 gm ,0.0125 mmol). The oxidation reactions were carried out under the same reaction conditions as that of cyclohexane and all the reactions were carried out for a period of one hour.

Phenol hydroxylation was carried out under atmospheric pressure. Thus phenol (1.88 gm, 20 mmol), H_2O_2 (2.36 gm, 20 mmol) are mixed together in 2.1 gm acetonitrile and catalyst (0.025 gm, 0.0125 mmol) . The reaction was carried out at 65^o C. Reaction parameters were varied to study the trends.

2.3 Procedures : Catalyst characterisation

2.3.1 Chemical analysis

The CHN analysis was done to determine the percentage of carbon, hydrogen and nitrogen present in the organic counter cation. The elemental analysis was done on Carlo Erba instrument (model no. EA 1108 elemental analyzer).

The other technique for chemical analysis included X-ray flourescence carried out on a sequential wavelength dispersive X-ray spectrometer (Rigaku, 3070 E).

Atomic absorption spectroscopy was done on an atomic absorption spectrometer Hitachi model Z- 8000. Standard solutions were used for calibration. Metals like V, Co, Mn and Cu were quntitatively estimated by this method.

2.3.2 Thermal analysis

This technique was used for determining the total number of water molecules present in heteropolycompound. The loss of weight corresponds to the loss of two different types of water molecules in the heteropolycompound. The thermal analysis was done on Seiko model instrument (TG/DTA 32). The rate of heating was kept at 10° C / minutes from 30°C upto 600°C under nitrogen atmosphere.

2.3.3 Infrared spectroscopy

The vibrational spectra of the samples were carried out to confirm the formation of the Keggin structure. The frequencies were indicative of the nature of the metal- oxygen bonds predominantly present in these type of complexes.

The FTIR spectra of the catalysts were recorded as nujol mulls at ambient temperatures between the range 4000 – 400 cm^{-1}. The spectra were recorded on a Shimadzu FTIR 8201 PC instrument.

2.3.4 UV-Visible spectroscopy

The electronic absorption spectra were recorded for structural and quantitative analysis. This kind of spectroscopy gives information about the electronic state of the compound.

The instrument in use was a Shimadzu UV-2101 PC UV – VIS spectrophotometer. The spectra were recorded at room temperature between the range 200 – 900 nm. The solution spectra were taken with reference to the respective solvent as the background. UV-Visible spectroscopy was useful for in situ characterisation of the reaction mixture for the determination and identification of the active intermediate species.

2.3.5 Electron paramagnetic resonance spectroscopy

This technique was used for determining the electronic state of the metal present in the heteropoly compound.

The solid and solution spectra were recorded at ambient temperatures on a Bruker EMX-X band spectrometer with 100 kHz modulation. The spin Hamiltonian parameters were determined by simulating the spectra using a Bruker Simfonia software package.

2.3.6 NMR spectroscopy

Structural elucidation of heteropoly complexes was achieved by this technique. It is a valuable tool to study the electron density distribution due to chemical shifts induced in the heteropoly compounds. Solid and solution NMR with ^{51}V, ^{13}C, nuclei was carried out on a Bruker instrument MSL 300. The measurements were carried out at 75.47 MHz for ^{13}C and 78.9 MHz for ^{51}V using a standard 10 mm probe. An external D_2O lock was used for all the measurements. The chemical shifts for ^{51}V used $VOCl_3$ as the external standard while for ^{13}C the standard was dioxane in D_2O.

2.3.7 Cyclic Voltammetry

This electrochemical technique is used for the study of redox active materials in heteropoly compounds. The transition metal substituted heteropoly compounds are studied for their redox behaviour by this method. Cyclic voltammetry is a tool to understand the rapid electron transfer between the metal ions. The feasibility of a particular reaction is dependent on the redox potential of the catalyst and the substrate. This can be easily determined using this technique.The cyclic voltammetry studies were carried out on an EG & G scanning potentiostat model attached with plotter model RE 0151.

CHAPTER –3

OLEFIN OXIDATION

3.0 Olefin oxidation

3.1 Introduction

Oxidation of olefins leads to the formation of products like epoxides, carbonyl compounds, diols which are of importance to both fundamental and industrial chemistry. The epoxides in particular find use in insecticides, plasticizers, resins, stabilizers for rubber and paints, lubricants, detergents, emulsifiers and waxes. Epoxy resins are used as coatings, adhesives, castings and foams.

The task of designing new catalysts for selective oxidation of olefins by heteropoly anions has been accomplished by the synthesis of transition metal substituted complexes [1,2]. Introduction of the transition metal into the Keggin structural framework of tungstophosphate enhances the oxidising power of the heteropoly anions. Thus transition metal ions such as Co^{2+}, Fe^{3+}, Ni^{2+}, Ru^{3+}, Cr^{3+}, Ti^{4+}, etc., have been incorporated into the Keggin structure by stepwise replacement of the tungsten atoms. It has been found by spectral evidences that the structural identity of the complex is retained even after such substitution. The major factor responsible for employing such compounds as oxidation catalysts is their relative stability towards oxidative degradation. Further, these catalysts are thermally stable and easy to prepare in high yields. Alkene epoxidation by dioxygen in the presence of isobutyraldehyde and tetrabutylammonium salts of transition metal substituted lacunary heteropoly anions $[PM(L)W_{11}O_{39}]^{(7-n)-}$ where [$M^{n+} = Co^{2+}$, Mn^{2+}, Cu^{2+}, Pd^{2+}, Ti^{4+}, Ru^{4+}, V^{5+}] and L = H_2O has been studied by Kholdeeva *et al* [3]. There are a few other reports about olefin epoxidation with oxygen and aldehydes using transition metal substituted poluoxometalates as catalysts [4-6]. In this chapter we describe the synthesis and catalytic study of the mono and di titanium substituted Keggin tungstophosphate anions, for the air oxidation of styrene and cyclohexene in presence of isobutyraldehyde.

Air oxidation of styrene and cyclohexene has been studied in the presence of isobutyraldehyde as reductant using HPA catalysts such as $K_5[PW_{11}TiO_{40}]$, $K_7[PW_{10}Ti_2O_{40}]$, $K_2[Bu_4N]_5[PW_{10}Ti_2O_{40}]$, $Na_{2.25}[(CH_3)_2(C_6H_5)(C_6H_5CH_2)N]_{4.75}[PW_{10}Ti_2O_{40}]$ [DMPBA salt] and $K_7[PW_{10}Ti_2O_{40}]$ supported (10% by wt.) on silica. The major product of styrene oxidation was styrene oxide while that for cyclohexene was the corresponding oxide. The maximum molar conversion for styrene was 81% with 83% selectivity for the oxide; for cyclohexene, these values were 49 and 93% respectively.

3.2 Experimental

3.2.1 Materials

Acetonitrile (HPLC grade) and other reagents were procured from Loba Chemie, Mumbai; cyclohexene and styrene (Aldrich) were used as such. The catalysts $K_5[PW_{11}TiO_{40}]$, $K_7[PW_{10}Ti_2O_{40}]$, $K_2[Bu_4N]_5[PW_{10}Ti_2O_{40}]$, $Na_{2.25}[(CH_3)_2(C_6H_5)(C_6H_5CH_2)N]_{4.75}[PW_{10}Ti_2O_{40}]$ and $K_7[PW_{10}Ti_2O_{40}]$ supported (10% w/w) on silica were prepared according to methods mentioned in chapter 2 and were characterised by elemental and thermal analysis, XRF and FTIR spectroscopy.

3.2.2 Procedure

A typical experimental procedure was as follows : Styrene (5.2 g, 5 mmol), cyclohexene (4.1 g, 5 mmol), isobutyraldehyde (14.42 g, 20 mmol), the solvent acetonitrile (15 ml) and the catalyst (65 micromols) were taken in a Parr pressure vessel (capacity 300 ml) and pressurised with dry air to 440 psi. The autoclave was heated to 60°C under stirring (600 r.p.m) and kept for 5 h. The product was taken out after releasing the gas at 10°C and analysed by gas chromatograph Hewlett Packard model 5890-II with a SE-30 megabore capillary column and equipped with flame ionisation detector.

3.3 Results and discussion

3.3.1 Catalyst characterisation

Thermal analysis

The thermal analysis of all catalysts was carried out to determine the number of water

molecules in the compounds.

$K_5PW_{11}TiO_{40}$

As can be seen from the thermogram (Fig- 1) the mass loss upto 150°C is due to water molecules and the final value of mass loss at 582.6°C was found to be 3.657%. This accounts for a total of 6 water molecules in the compound.

$K_7PW_{10}Ti_2O_{40}$

The thermogram in Fig –1 shows a single decomposition step upto 200°C due to loss of water, and beyond 250°C, it shows no weight loss. The total mass lost is 7.439% accounting for 13 water molecules.

$K_2[Bu_4N]_5[PW_{10}Ti_2O_{40}]$

In the thermogram (Fig –1) the loss in the weight due to water molecules has been observed upto 200°C. The weight loss in percentage due to water at this stage is 7.52% which corresponds to 18 water molecules. The weight loss due to organic moiety begins from 200 and ends at 400°C and thereafter there is no loss in weight.

$Na_{2.25}[(CH_3)_2(C_6H_5)(C_6H_5CH_2)N]_{4.75}[PW_{10}Ti_2O_{40}]$

This compound shows a loss in weight (Fig.1) due to water molecules upto 116.9°C which corresponds to 1.77% and the total water molecules calculated to be ≈ 4. The remaining three decomposition steps seen at 218.9, 288.6 and 379.9°C are due to loss in weight because of the different organic groups present in the counter cation.

Elemental analysis

The carbon, hydrogen and nitrogen percentages in the tetrabutyl and the DMPBA salt was determined by microanalysis.

$K_2[Bu_4N]_5[PW_{10}Ti_2O_{40}]$:Carbon – 24.23 (24.66), Nitrogen – 1.69 (1.79), Hydrogen – 4.41 (4.62) Oxygen- 21.91 (22)

$Na_{2.25}[(CH_3)_2(C_6H_5)(C_6H_5CH_2)N]_{4.75}[PW_{10}Ti_2O_{40}]$:Carbon – 22.88 (23.11), Nitrogen – 1.61 (1.79), Hydrogen – 2.35 (2.50) Oxygen – 18.77 (18.87)

The values in bracket are the calculated %.

XRF analysis

X-ray fluorescence technique was used to calculate the amount of titanium, phosphorus and tungsten in the freshly prepared complexes. Pellets of the catalysts were prepared and calibration was done by preparing a standard pellet containing TiO_2, WO_3, KH_2PO_4 of comparable composition. NaH_2PO_4 was used instead of KH_2PO_4 for the DMPBA salt. The % composition was found to be as follows

$K_5[PW_{11}TiO_{40}]$: K- 5.99 (6.41), P – 0.99 (1.03), W – 65.99 (66.37), Ti – 1.48 (1.58)

$K_7[PW_{10}Ti_2O_{40}]$:K- 8.69 (8.78), P – 0.89 (0.99), W – 58.88 (59.13), Ti – 2.96(3.06)

$K_2[Bu_4N]_5[PW_{10}Ti_2O_{40}]$:K- 1.80 (1.85), P – 0.68 (0.73), W – 42.88 (43.67), Ti – 2.06 (2.26)

$Na_{2.25}[(CH_3)_2(C_6H_5)(C_6H_5CH_2)N]_{4.75}[PW_{10}Ti_2O_{40}]$:Na- 1.29 (1.39), P – 0.78 (0.83), W – 49.01 (49.70), Ti – 2.46 (2.57)

The values in bracket are the calculated %.

Infrared spectra

The IR spectra of the catalysts (Table –1) shows absorption peaks between 1100 and 800 cm^{-1} which are characteristic of Keggin units. The triply degenerate asymmetric phosphate stretch at 1080 cm^{-1} in phosphotungstic acid is split for mono-substituted complex (at 1049 and 1082 cm^{-1}) and into three peaks for di-substituted complex (at 1082, 1062 and 1045 cm^{-1}). These splittings are caused by the lowering of the tetrahedral site symmetery by the replacement of $[W^{VI}O]^{4+}$ sub-units by titanium; the degree of splitting varies with the nature of the heteropoly group, and the strength of the bond between W-O and P-O groups [7,8].

Table -1
FTIR spectral details of the catalysts
used in the reactions

Catalyst	υP-O	υW-O_t	υW-O_c-W	υW-O_e-W
$K_5[PW_{11}TiO_{40}]$	1049 1082	952	860	796
$K_7[PW_{10}Ti_2O_{40}]$	1082 1062 1045	954	875	796
$[Bu_4N]_5K_2$ $[PW_{10}Ti_2O_{40}]$	1068	972	848	805
$Na_{2.25}$ $[DMPB]_{4.75}$ $[PW_{10}Ti_2O_{40}]$	1055	950	889	808
$H_3[PW_{12}O_{40}]$	1078	979	902	808

c = corner sharing
e = edge sharing

3.3.2 Catalytic activity

Styrene oxidation

Styrene oxidation, carried out air in presence of excess of isobutyraldehyde and PWTi as catalyst, proceeds under mild conditions to give epoxide and isobutyric acid as main oxidation products. Among the catalysts studied, both $K_5PW_{11}O_{40}$ and $K_7PW_{10}Ti_2O_{40}$ give almost the same styrene conversions (about 70%). A marginal increase in the epoxide selectivity (about 77%) has been observed for the disubstituted analogue. Both the quaternary ammonium salts of disubstituted PWTi catalysts give a decreased styrene conversion compared to the corresponding potassium salts. The epoxide selectivity using DMPBA salt was found to be higher than that of Bu_4N derivative. The enhanced catalytic activity observed for the silica supported $KPWTi_2$ catalyst could be attributed to an increased surface area of the catalyst.

Results are given in Table 2.

Table - 2

Oxidation of styrene by titanium containing tungstophosphates

Catalyst (in mmol)	Molar Conv.%	Product Sel. %		TON
		Oxide	C_6H_5CHO	

$K_5[PW_{11}TiO_{40}]$ [0.06569]	69.0	71.3	28.7	106
$K_7[PW_{10}Ti_2O_{40}]$ [0.06578]	70.0	76.7	23.3	106
$[Bu_4N]_5K_2$ $K_7[PW_{10}Ti_2O_{40}]$ [0.06578]	56.0	58.1	41.9	85.0
$Na_{2.25}[DMPB]_{4.75}$ $[PW_{10}Ti_2O_{40}]$ [0.06578]	57.0	73.7	26.3	86
Supported $K_7[PW_{10}Ti_2O_{40}]$ / SiO_2 (10 % w/w) [0.0328]	81	83.2	16.7	247.0
$K_7[PW_{10}Ti_2O_{40}]$ Without aldehyde [0.06578]	20.5	-	100	31.0
$H_3[PW_{12}O_{40}]$	6.8	-	100	

Cyclohexene oxidation

The second substrate for study was cyclohexene. The results are summarised in Table 3. As in the case of styrene, the major product of its oxidation was cyclohexene oxide with minor quantities of allylic oxidation products such as 2-cyclohexene-1-ol and 2-cyclohexene1-one, identified by GC-MS (Shimadzu model QP 5000) and estimated by GC using standard reference samples. The results show that supported catalyst gives maximum conversion (about 47%) compared to the neat HPA salts. However the selectivity for epoxide was higher in the case of neat complexes.

Table –3 gives the results for cyclohexene oxidation.

Table - 3

Oxidation of cyclohexene by titanium
containing tungstophosphates

Catalyst (in mmol)	Molar Conv.%	Product Sel. %			TON
		Oxide	2- ol	2-one	
$K_5[PW_{11}TiO_{40}]$ [0.06569]	39.9	88.3	1.8	9.9	61
$K_7[PW_{10}Ti_2O_{40}]$ [0.06578]	42.8	89.8	0.9	9.3	65
$[Bu_4N]_5K_2$ $K_7[PW_{10}Ti_2O_{40}]$ [0.06578]	37	92.2	5.1	2.7	56
$Na_{2.25}[DMPB]_{4.75}$ $[PW_{10}Ti_2O_{40}]$ [0.06578]	49.0	93	3.3	3.7	59
Supported $K_7[PW_{10}Ti_2O_{40}]$ / SiO_2 (10 % w/w) [0.0328]	47.0	78.5	69.0	14.6	143.0

When the oxidation of styrene was carried out without the addition of isobutyraldehyde, the product obtained was mainly benzaldehyde at 20% conversion. Isobutyraldehyde was oxidized to the corresponding acid and was estimated by gas chromatography.

In order to ascertain the function of titanium in HPA catalysed aerial oxidation of olefins, a control experiment was carried out using styrene as substrate and phosphotungstic acid as catalyst. In this reaction, benzaldehyde was the main product and the conversion was about 7%, thus confirming that the presence of titanium is important for the selective epoxidation reaction and that the transition metal centers are active sites for the reaction.

The structural stability of the Keggin type titanium substituted tungstophosphates under the reaction conditions is an important criteria for the studies. The FTIR spectrum of the catalyst $K_7PW_{10}Ti_2O_{40}$ were compared before and after the reaction. It was observed that both were almost identical; all the absorption peaks characteristic of the Keggin structural framework (between 1100 and 800 cm^{-1}) were retained after the reactions as seen in figure 2. This observation indicates that these compounds are robust oxidation catalysts which retain their structure during the course of the oxidation process.

In order to understand the reaction mechanism, two parallel experiments were conducted, one by the addition of a radical trapping anti-oxidant (diphenyl amine, 5 mmol) to the reaction mixture containing cyclohexene (50 mmol), isobutyraldehyde (200 mmol and $K_7PW_{10}Ti_2O_{40}$ (0.065 mmol) in acetonitrile (15 ml) in presence of oxygen and other experiment without anti-oxidant. No oxidation products were obtained in the case of diphenyl amine added experiment which suggests a chain radical mechanism via acyl peroxy radical formation leading to epoxide and isobutyric acid as suggested by Kholdeeva *et al*. Less than one percent cyclohexene conversion with a negligible amount of epoxide and isobutyric acid were noticed in the reaction products of former experiment compared to a 40% conversion with 90% selectivity in the case of latter [3].

The reaction mechanism comprises elementary steps of chain radical process leading to epoxide and isobutyric acid formation.

The acyl peroxy radicals are the active intermediates in epoxidation reactions. These are generated *via* reaction 5 if the oxidation reaction is carried out in the presence of complexes which catalyse the homolytic decomposition of peroxy acid.

3.4 Conclusions

In this chapter we have reported results for the highly selective aerial epoxidation of olefins - styrene and cyclohexene - catalysed by titanium substituted tungstophosphates.

The usage of isobutyraldehyde as the reductant improved conversion and selectivity to the desired products, namely the oxides. It was proven beyond doubt that the oxidation reaction proceeds *via* the radical chain mechanism with the acyl peroxy radical as the active intermediate involved.

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CHAPTER – 4

OXIDATION OF *P*- XYLENE

4.0 Oxidation of para - xylene

4.1 Introduction

4.2 Experimental

4.3 Results and discussion

4.4 Conclusions

4.5 References

4.1 Introduction

The oxidation of alkyl benzenes to the corresponding carboxylic acids is of industrial importance. Oxidation of para - xylene to yield the completely oxidized product i.e., terephthalic acid, is an important industrial process. Terephthalic acid is useful in the manufacture of a polyester, polyethylene terephthalate. The industrial preparation of aromatic polyesters requires a cheap source of aromatic acids. This polyester is formed by the condensation of terephthalic acid and ethylene glycol. Polyethylene terephthalate can be fabricated into an excellent fiber. This led to a search to find a suitable reagent of sufficient availability and a suitable oxidation method to prepare terephthalic acid. The key idea was to find a catalyst which will selectively control the incorporation of dioxygen into the hydrocarbon. Other uses of terephthalic acid include the manufacture of paints, films and adhesives. Due to the extreme insoluble and non-melting nature of terephthalic acid it cannot be prepared on a large scale with purity sufficient enough for condensation with ethylene glycol to produce the polyester. The crude terephthalic acid is therefore converted into dimethyl ester i.e., dimethyl

terephthalate, which is then brought to the fiber grade by crystallization and distillation. Many intermediate products of oxidation are formed in this reaction which include para - tolualdehyde, para - toluic alcohol, para - toluic acid, 4 - carboxybenzaldehyde, 4 - carboxybenzyl alcohol and terephthalic aldehyde. The intermediate product 4 - carboxybenzaldehyde is the most deleterious contaminant formed during the manufacture of terephthalic acid as this aldehyde group is unable to undergo polymerization with ethylene glycol during polyethylene terephthalate formation. The aerial oxidation of para - xylene proceeds in acetic acid medium in the presence of Co-Mn-Br catalyst to produce terephthalic acid. Various catalytic procedures for this oxidation of para - xylene to terephthalic acid have been described in patent literature as this is an industrially important reaction. US patent No. 4892,970, assigned to Amoco Corporation, describes a process for the oxidation of para - xylene selectively to terephthalic acid in the presence of a mixture of cobalt acetate, manganese acetate and HBr as catalysts and acetic acid as solvent. Zaidi has reported the use of low concentrations of cobalt acetate and sodium bromide as catalysts in the liquid phase oxidation of para - xylene by air at a temperature of 60-105^{o} to afford only para - toluic acid [1]. A major disadvantage of the above described process is the necessity to combat the corrosive nature of cobalt/ manganese/ bromide/ acetic acid mixtures and consequent increase in cost of capital equipment due to the usage of expensive anti- corrosive Teflon coated autoclave. Another disadvantage is the loss of about 10 parts by weight of acetic acid per 100 parts of aromatic carboxylic acid produced, by conversion to carbon dioxide. Other reports on oxidation of para -xylene include the use of transition metal salts of Fe^{3+}, Cu^{2+}, Ni^{2+} or Cr^{3+} in combination with cobalt salts as catalysts. Cobalt catalyzed para - xylene oxidation in aqueous medium at temperature in the range 100-150 °C in the presence of phase transfer catalysts has also been reported. This process yielded mainly para - toluic acid as the oxidation product [2]. In this chapter we report the liquid phase oxidation of para - xylene using transition metal substituted Keggin type heteropoly anion in a halide free system in aqueous medium to give a mixture of para - toluic and terephthalic acids.

4.2 Experimental

4.2.1 Materials

Para-xylene, 1,2-dichloroethane and 70% aqueous tert- butyl hydroperoxide were procured from Aldrich and were used as such for the reactions. The catalysts were prepared according to methods described in chapter 2. The catalyst characterisation was done by techniques like thermal analysis, atomic absorption, infrared, electron spin resonance (ESR) and UV – Visible spectroscopy .

4.2.2 Procedure

The reaction was carried out in a stainless steel 300 ml capacity Parr autoclave. The reactants, para - xylene (15 g, 140 mmol), water (15 g), tert-butyl hydroperoxide as the initiator (0.3 g) and the catalyst (0.096 mmol) were taken in the autoclave. The reactor was pressurised with air upto 400 psi and kept at 180° with stirring (600 rpm). After an induction period of 2 h, a sudden drop in pressure was observed suggesting the commencement of the oxidation reaction; heating and stirring were maintained till there was no further pressure drop. The autoclave was then cooled to 0^oC and gaseous products were released through a gas holder, collected and analysed. The reactor was further repressurised with air upto 400 psi and the reaction was continued at 180^oC. This operation was repeated once more. The solid product (6.5 g) was separated by filtration. A sample of the solid product was analysed after esterification by the following procedure: the solid product (0.1g) was dissolved in methanol (5 ml) and to that was added BF_3.MeOH (14% solution, 2 ml) and the mixture was then refluxed for 6 h. After cooling the sample, water was added and the esters formed were extracted with dichloromethane and analysed by GC. The filtrate portion of the oxidation product consisted of the aqueous and the organic layer. Both the layers were separated. The aqueous layer was extracted with small volume of dichloromethane and mixed with organic layer and analysed.

Analysis of products : The gaseous products were analyzed on a Shimadzu GC- 14B with thermal conductivity detector having Porapak N column. The liquid oxidation products were analyzed on Hewlett Packard GC, model 5890 using SE-52 megabore capillary column for separation.

4.3 Results and discussion

4.3.1 Catalyst characterisation

Thermal analysis

The water content in the $K_5[PW_{11}Co(H_2O)O_{39}]$, $K_5[PW_{11}Mn(H_2O)O_{39}]$, $K_5[PW_{11}Cu(H_2O)O_{39}]$, $K_6[SiW_{11}Co(H_2O)O_{39}]$, $K_6[SiW_{11}Mn(H_2O)O_{39}]$

and $K_6[SiW_{11}Cu(H_2O)O_{39}]$ was determined by thermogravimetric analysis.

Constitutional water is present in all the above catalysts. This water is lost upto ≈ 550°C while heating the catalyst upto 600°C.

$K_5[PW_{11}Co(H_2O)O_{39}]$

The loss due to water takes place at three different temperatures till 600°C. The final weight loss corresponds to 9.325% which when calculated accounts for ≈ 17 water molecules.

$K_5[PW_{11}Mn(H_2O)O_{39}]$

The loss in weight due to water molecules is noticed upto 11.02% which is equivalent to 20 water molecules in the complex.

$K_5[PW_{11}Cu(H_2O)O_{39}]$

The different decomposition steps amount to a total of 11.14% weight loss which when calculated accounts for 20 water molecules in the compound. $K_6[SiW_{11}Co(H_2O)O_{39}]$

Two steps of degradation are seen for the cobalt substituted complex, one at 136.9°C and the other at 588°C. The final weight loss is recorded as 10.54% which shows 19 water molecules in the complex.

$K_6[SiW_{11}Mn(H_2O)O_{39}]$

The compound is thermally stable with complete weight loss occurring at 582.7°C equivalent to 9.16%. This corresponds to 17 water molecules.

$K_6[SiW_{11}Cu(H_2O)O_{39}]$

The total weight loss occurs at 587.9°C which is equivalent to 8.023% loss corresponding to 14 water molecules.

The thermograms are given in figure –1.

Atomic absorption spectroscopy

The quantitative analysis of the elements incorporated in the heteropoly compounds were determined by atomic absorption spectroscopy. The aqueous solutions of the catalysts with appropriate concentrations ($\approx$ 100 ppm) were given for atomic absorption spectroscopy and the percentages of the substituted metals were determined. In table-1 are listed the concentrations of the substituted transition metals

Table-1

Concentrations of the substituted transition metals

Catalyst	% Metal (theoretical value)
$K_5[PW_{11}Co(H_2O)O_{39}].17H_2O$	1.63 (1.81)
$K_5[PW_{11}Mn(H_2O)O_{39}].20H_2O$	1.44 (1.66)
$K_5[PW_{11}Cu(H_2O)O_{39}].20H_2O$	1.78 (1.91)
$K_6[SiW_{11}Co(H_2O)O_{39}].19H_2O$	1.56 (1.76)
$K_6[SiW_{11}Mn(H_2O)O_{39}].17H_2O$	1.42 (1.67)
$K_6[SiW_{11}Cu(H_2O)O_{39}].14H_2O$	1.74 (1.95)

Infrared spectroscopy

IR spectra of the transition metal substituted phosphotungstate complexes show the absorption bands characteristic of Keggin structure, viz. peaks at 1074 cm^{-1}, 943 cm^{-1}, 920 cm^{-1} and 810 cm^{-1} respectively due to ν $[P\text{-}O\text{-}(W_a)]$, ν ($W\text{-}O_b$) and the two ν ($W\text{-}O_c\text{-}W$) where a = central P-O bond, b = terminal double bond between tungsten and oxygen and c = the two types of bridging bonds between metal – oxygen – metal [3]. Further the presence of a shoulder near 1074 cm^{-1} could be attributed to the stretching frequency of P-O-(M) bond, thus indicating the presence of transition metal ion in the heteropolyanion. The IR spectra of the analogues silicotungstate salts exhibited peaks

at 1000, 960, 900 and 796 cm^{-1} which were attributed respectively to ν(W-Ot), ν(Si-O-W) and to the types of bridging (W-O-W). The transition metal absorption could not be resolved as these absorptions overlap with the (W-O-W) band.

The FTIR spectra of the catalysts are shown in figure - 2 .

ESR spectroscopy

The copper and manganese containing heteropoly compounds were shown to be ESR active, with these metals in the +2 oxidation state. The spectra of the powdered samples were taken at room temperature i.e. 298 K.

ESR spectrum of $K_5PW_{11}Mn(H_2O)O_{39}$

The ESR spectrum of $K_5PW_{11}Mn(H_2O)O_{39}$ exhibit signals at 1940 G, 4983 G, 1525 G, 2250 G, 3453 G. All these features indicate Mn – Mn dimeric interaction in the Keggin structure of the compound. Had it been one manganese center in Keggin unit one would have observed a signal at 3475 G (corresponding to $g \approx 2$) only.

ESR spectrum of $K_6SiW_{11}Mn(H_2O)O_{39}$

The spectrum exhibits interacting manganese signals at 1073 G and 3669 G. However, the difference in the spectra of $K_6SiW_{11}Mn(H_2O)O_{39}$ and $K_5PW_{11}Mn(H_2O)O_{39}$ suggests that the Mn – Mn species are of different nature in the two compounds.

ESR spectrum of $K_5PW_{11}Cu(H_2O)O_{39}$

Two types of species were known to be present in the copper substituted complex. Copper is seen to be present in the monomeric and dimeric form.

Copper in the monomeric form

Copper present in the monomeric state was found to have the following ESR parameters:

$A_{||}$ = 94. 79 G, $g_{||}$ = 2.408, $g_{\perp}$ = 2.077. The $A_{\perp}$ parameter was not resolved.

Copper in the dimeric form

The signals at 2427 G, 3692 G, 3967 G were found to be due to the spin allowed transitions of dimeric copper interactions. Yet another signal at 1554 G is due to forbidden transition ($\Delta M_s = \pm 1$) of the dimeric Cu (II) species.

ESR spectrum of $K_6SiW_{11}Cu(H_2O)O_{39}$

The ESR spectrum of copper in the silicotungstate framework shows copper present as monomeric and the dimeric species.

Monomeric copper

Copper in the monomeric form has the following ESR parameters

$A_{||}$ = 103.8 G, $g_{||}$ = 2.383 and 2.361. There are two different $g_{||}$ values suggesting the presence of more than one type of monomeric copper.

The $A_{\perp}$ parameter is not resolved while $g_{\perp}$ = 2.105 for both the types of monomeric species.

Additional signals at 1550 G, 2521 G and 3679 G are due to dimeric copper species present in the compound.

The ESR spectra are given in figure 3.

UV – Visible spectroscopy

Cobalt in the +2 oxidation state was shown to be EPR inactive and hence its incorporation in the Keggin framework was proven by UV – Visible spectroscopy.

The UV-Visible spectra of these catalysts were taken in water medium. The spectrum of the cobalt substituted phosphotungstate catalyst exhibited absorption band at 530 nm because of the typical *d-d* transitions. The cobalt substituted silicotungstate also showed corresponding band at 546 nm. The UV- Vis spectra are shown in fig.4.

Fig.4 UV-Visible spectra of (a) $K_5PW_{11}Co(H_2O)O_{39}$
(b) $K_6SiW_{11}Co(H_2O)O_{39}$

4.3.2 Catalytic activity

The transition metal substituted heteropolyanions of the type $K_5[PW_{11}M(H_2O)O_{39}]$ and $K_6[SiW_{11}M(H_2O)O_{39}]$ (M = Co^{2+}, Mn^{2+} and Cu^{2+}) have been found to be good catalysts for the aerial oxidation of para - xylene in water medium. Oxidation reactions were carried out under identical conditions using these catalysts and the results are tabulated in Table-2. The results reveal that the silicotungstate analogues give 10-20%

more catalytic efficiency for para - xylene conversion compared to phosphotungstate analogues. Among the catalysts studied the cobalt substituted silicotungstate, $K_6[SiW_{11}Co(H_2O)O_{39}].19\ H_2O$ gives maximum activity as seen from the higher para - xylene conversion. Under the set experimental conditions, the major oxidation product was para - toluic acid. Other products included para - tolualdehyde, para - methyl benzyl alcohol and terephthalic acid.

Table- 2

Air oxidation of *p*-xylene catalysed by transition metal substituted heteropolyanions

Catalyst	Conversion mol%	Product selectivity %			
		A	B	C	D
$K_5PW_{11}Co(H_2O)O_{39}$	52.28	61.65	21.45	15.45	0.99
$K_5PW_{11}Mn(H_2O)O_{39}$	54.36	68.42	21.74	9.83	-
$K_5PW_{11}Cu(H_2O)O_{39}$	50.01	51.39	24.72	18.82	5.05
$K_6SiW_{11}Co(H_2O)O_{39}$	70.45	60.64	24.53	13.27	1.54
$K_6SiW_{11}Mn(H_2O)O_{39}$	51.13	65.04	22.21	11.27	1.46
$K_6SiW_{11}Cu(H_2O)O_{39}$	65.72	52.53	23.00	23.62	0.85

Reaction temp.180^o, *p*-xylene 15 g, water 15 g. A: para- toluic acid; B: para - tolualdehyde; C: para - methyl benzyl alcohol; D: terephthalic acid

The effect of different reaction parameters such as temperature, catalyst concentration and solvent were studied on the oxidation of para – xylene using the catalyst $K_6[SiW_{11}Co(H_2O)O_{39}].19H_2O$.

Effect of temperature

Oxidation of para - xylene was carried out using the catalyst $K_6[SiW_{11}Co(H_2O)O_{39}].19H_2O$ at a temperature range 140 –180°C; the results [given in table-3] suggest an increased product yield at 180°C. The conversions were much less upto 160°, thereafter a sudden increase in the reaction rate was observed. At lower temperatures the first oxidation products such as para - methyl benzyl alcohol and tolualdehyde were more than para - toluic acid. At 180°C, there was a sudden increase in the yield of terephthalic acid in the product suggesting that the catalyst was very effective even at this temperature and did not undergo any decomposition.

Table-3

Effect of temperature on para - xylene conversion.

Temp (°C)	Conversion Mol %	Product selectivity %			
		A	B	C	D
140	12.67	19.67	37.39	42.92	-
160	32.22	35.93	30.29	33.76	-
180	70.45	60.64	24.53	13.27	1.54

A, B, C and D same as in table-2.

Effect of catalyst concentration

The effect of catalyst concentration on the oxidation of para - xylene has been studied. The oxidation reactions were performed at 180°C using three different molar ratios of para - xylene and $K_6[SiW_{11}Co(H_2O)O_{39}].19H_2O$ under identical conditions. The data given in table-4 suggest that there has been a significant increase in the reactivity at molar ratio 1470 as seen from the substrate conversion value. At higher catalyst concentration, there was a drastic reduction in para - xylene conversion which would be attributed to the inhibiting action of the catalyst. Transition metal complexes are known to be good catalysts for side chain oxidation reactions at low concentration levels, but as inhibitors at higher concentrations [4].

Table- 4
Effect of catalyst concentration on
para - xylene conversion

Catalyst conc. (substrate to catalyst molar ratio)	Conversion mol %	Product selectivity %			
		A	B	C	D
735	27.97	43.31	21.67	34.77	-
1100	57.64	63.67	19.59	16.72	-
1470	70.45	60.64	24.53	13.27	1.54

A , B, C,D same as in Table-2

Effect of solvent

The oxidation of para - xylene has been carried out at 180° using 1,2-dichloroethane and water as solvents, a solventless reaction also has been carried out [Table-5]. The solventless reaction gave a low (≈25%) conversion, though the selectivity to para - toluic acid was high (72.15%). The selectivity to other products, i.e., para -tolualdehyde and para - methyl benzyl alcohol is 23.52% and 4.31% respectively.

The reaction in 1,2-dichloroethane also gave a poor conversion of ≈20%. No para -methyl benzyl alcohol was formed in this reaction the products formed were para -toluic acid and para - tolualdehyde with 62.3 and 37.69% selectivity respectively. When water was used as medium , the conversions were increased upto 70 %. The difference in conversion in various solvents may be attributed to the polarity of the solvents. Mobility of the free radicals, the active species in this autoxidation reaction, would be more in polar solvents such as water. Hence the conversion values for para - xylene were found to be more in aqueous media.

Table-5

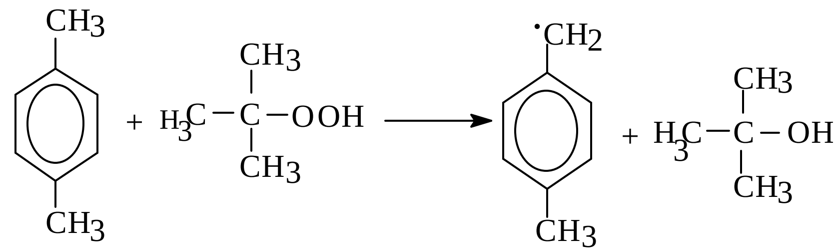
Effect of solvent on para - xylene conversion

	Conversion mol %	Product selectivity %			
Solvent		A	B	C	D
Solventless	25.71	72.15	23.52	4.31	-
1,2-Dichloroethane	20.37	62.30	37.69	-	-
Water	70.45	60.64	24.53	13.27	1.54

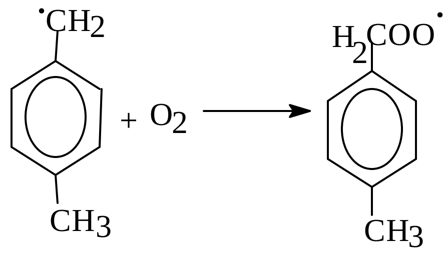
A, B, C, D same as in Table-2.

Reaction mechanism for *p*-xylene oxidation

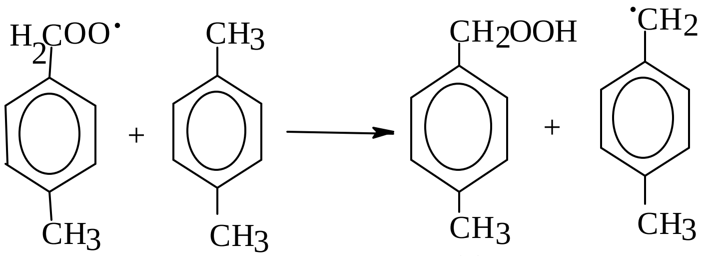
The hydrocarbon substrate, *p*-xylene reacts initially with the radical initiator, TBHP, to form the benzyl radical **(1)** which reacts with molecular oxygen to form benzyl peroxy radical **(2)**. The peroxy radical abstracts one hydrogen atom from *p*-xylene to give 4-methyl benzyl hydroperoxide **(3)**. This reaction is made more feasible in the presence of catalysts containing transition metals like Co^{2+}, Mn^{2+} and Cu^{2+}. This active transition metal centre reacts with benzyl hydroperoxide to form the species **(4)**, 4- methyl benzyloxy radical and an oxidized metal species. This oxidized metal reacts with benzyl hydroperoxide to get back to its original oxidation state along with the formation of active benzyl peroxy radical, which attacks another mole of substrate to continue the reaction. Meanwhile species **(4)** reacts with another mole of substrate to form the active benzyl radical and the cycle of reactions is repeated as seen in the reaction mechanism.



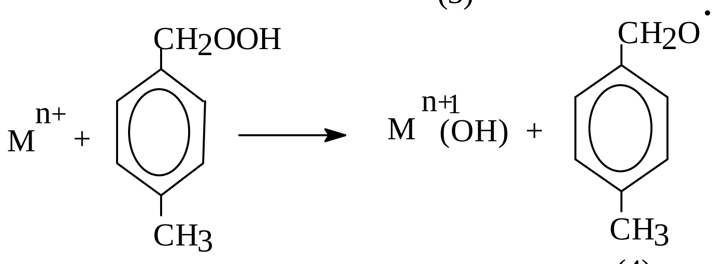
(1)



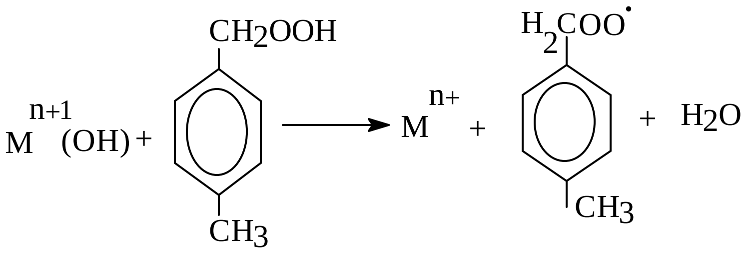
(2)

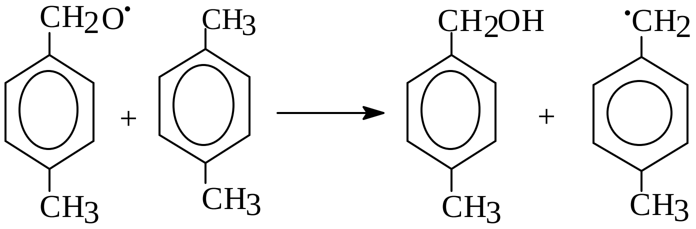


(3)



(4)




CH2O•
CH3
+
CH3
CH3
CH2OH
CH3
+
•CH2
CH3

4.4 Conclusions

The oxidation of *p*-xylene is an industrially important chemical reaction. The production of terephthalic acid from *p*-xylene is achieved in industry using an homogeneous cobalt - manganese based catalyst with bromine compounds as promotors in acetic acid medium. In this chapter we discuss the utility of cobalt, manganese and copper substituted silicotungstates as catalysts in *p*-xylene oxidation in aqueous medium with air as oxidant. The advantage of our system is that it has been performed under mild and non-corrosive conditions. The product obtained in the first stage of oxidation is *p*-toluic acid, which is an intermediate in the formation of terephthalic acid.

4.5 References

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3. R.O. Claude, D. Cchiccioli and T. Rene, J. Chem. Res (S)., (1977) 46.
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CHAPTER – 5

BENZENE HYDROXYLATION

5.0 Benzene Hydroxylation

5.1 Introduction

Phenol is produced commercially by Hock process, in which cumene is oxidised to cumene hydroperoxide by air oxidation in aqueous emulsion of Na_2CO_3 and its subsequent cleavage in acidic media to equimolar amounts of phenol and acetone [1]. The economy of this process is dependent on the market value of the side product acetone. Thus efforts are in progress for the development of a new route towards phenol synthesis via a one-step process by the hydroxylation of benzene to phenol. The hydroxylation of relatively inert hydrocarbons like benzene has remained an intriguing reaction and extensive research work has been focussed on the development of an efficient catalyst system for this purpose.

Many transition metal containing catalytic systems have been used for this type of oxidation reaction. The most common catalyst systems under operation include zeolites and transition metal complexes. Catalytic amounts of transition metal substituted polyoxometalates and mixed addenda complexes are found to be efficient for oxidation of hydrocarbons [2]. These complexes are able to oxidize hydrocarbons with a wide variety of oxygen donors. Literature is rich in reports for the use of transition metal substituted and mixed addenda containing catalytic systems for the hydroxylation of benzene mostly operable under homogeneous reaction conditions. The guest transition metal act as efficient oxygen transfer agents. The latter half of last decade has witnessed tremendous focus being laid on the use of such complexes for phenol synthesis from benzene. The main oxidants in use include hydrogen peroxide and molecular oxygen.

The tetrabutyl ammonium salts of iron and chromium containing tungstophosphates were found to be efficient as catalysts for the oxidation with hydrogen peroxide. Spectral techniques are used to detect the active intermediate species which are known to be formed by the interaction of the heteropoly containing the transition metal and the intermediate product of hydrogen peroxide decomposition [3,4]. Polyoxometalates containing the transition metals such as iron, chromium, ruthenium, vanadium and titanium are used as catalysts with hydrogen peroxide for benzene hydroxylation. The nature of heteropolyanion and composition of the reaction mixture are found to be the governing features for the catalytic activity [5]. The vanadium containing phosphomolybdates and phosphotungstates are equally efficient for the oxidation of benzene using hydrogen peroxide as oxidant under different reaction conditions [6-10]. Many spectroscopic techniques are used to identify the active intermediate species formed during the oxidation reaction. Transition metal containing polyoxometalates are functional as catalysts for benzene oxidation with molecular oxygen. Iron containing system was effective catalyst in the presence of molecular oxygen [11]. The use of heteropolyacids as reoxidants for metals like palladium and platinum have been reported for phenol formation with molecular oxygen [12,13].

The catalytic activity of mono, di and tri vanadium substituted molybdophosphates for the hydroxylation of benzene under improved reaction conditions to yield phenol in good yields has been reported in this chapter. The effect of the number of vanadium centers on the catalytic activity and the subsequent *in situ* spectroscopic study are reported in this part of the thesis.

5.2 Experimental

5.2.1 Materials

Benzene, aqueous 30 % hydrogen peroxide (E. Merck, India Ltd., India), acetonitrile of high purity grade were used as such without further purification. Strength of hydrogen peroxide was determined by redox titration with $KMnO_4$ prior to use in the oxidation reaction. Phosphomolybdic acid was used as such. The catalysts with the abbreviations $PMo_{11}V$, $PMo_{10}V_2$ and PMo_9V_3 were prepared by the methods described in chapter 2.

5.2.2 Procedure

Procedure for determination of strength of hydrogen peroxide

Hydrogen peroxide (5.5 gm) was taken in a 250 ml capacity volumetric flask and diluted up to the mark with distilled water. A definite volume of the diluted system (25 ml) was taken in a conical flask to which was added 20 ml each of 2N H_2SO_4 and distilled water. This solution was titrated against previously standardized $KMnO_4$. The end point of the titration was colourless to pink. From the titration reading the strength of hydrogen peroxide was calculated using the equation

$$\%\ \text{peroxide} = \frac{\text{Burette reading} \times \text{Normality of } KMnO_4 \times 25 \times 0.01701 \times 100}{\text{Weight of hydrogen peroxide taken}}$$

Procedure for catalytic run

The oxidation reactions were carried out in a two-necked 50 mL round bottom flask placed in an oil bath maintained at 338 K. In a typical experiment, 0.05 g (0.025 mM) of catalyst, 1.56 g (20 mM) of benzene and 2.36 g (20 mM) of aqueous hydrogen peroxide were mixed in 6 mL of acetonitrile and placed in the flask and the contents were stirred with a magnetic stirrer. The reaction mixtures, withdrawn at regular interval of 30 minutes, were analysed.

Analysis of products: The products of benzene hydroxylation were analyzed by a gas chromatograph (Hewlett Packard gas chromatograph model No. 5890 Series-II) using HP-5 fused column with 30m x 0.53m x 1.0 μm film thickness and FID detector. Phenol formed in the reaction was confirmed by comparing the retention time (standard) and also by GCMS (Shimadzu GC MS QP 5000). From the moles of benzene reacted, turnover numbers were calculated. The samples were also analysed simultaneously by UV- Visible and EPR spectroscopy to identify the active intermediate species.

5.3 Results and Discussion

5.3.1 Catalytic activity

The catalytic activities of vanadium substituted phosphomolybdic acids were investigated in the hydroxylation of benzene to phenol and the results are presented in Table 1. The hydroxylation of benzene gave phenol as the only product under the reaction conditions studied.

Table 1. Catalyst activities in hydroxylation of benzene to phenol[a]

Catalyst	Benzene conv.(mol.%)	TON
$PMo_{11}V$	10.7	92
$PMo_{10}V_2$	9.2	74
PMo_9V_3	6.3	50
$PMo_{12}O_{40}$	_	_

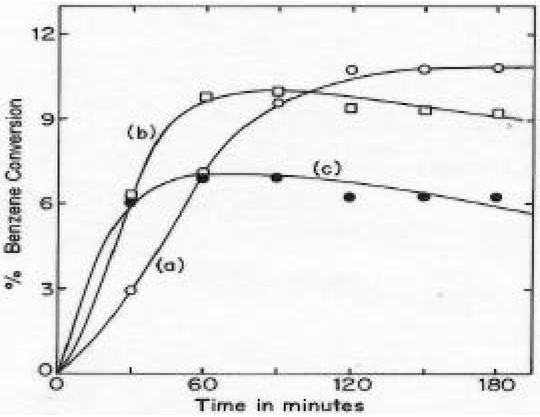
[a] Conditions: Benzene(0.02 M), H_2O_2(0.02 M), Catalyst(0.05 g), Acetonitrile (6 mL), Temperature (338 K), Reaction time (2 h) and TON = Turnover number (moles of benzene converted per mole of catalyst).

The maximum conversion of benzene (≅11%) with TON = 92 was achieved with $PMo_{11}V$. However, when the hydroxylation was carried out with free phosphomolybdic acid, no hydroxylation activity was seen. This confirms that vanadium is the active center in the above catalysts. The conversion of benzene increases linearly with all the catalysts and then becomes stable with further no change in the activities of catalysts. It is found that the activities of the three catalysts in hydroxylation of benzene to phenol decreased in the following order.

$PMo_{11}V > PMo_{10}V_2 > PMo_9V_3$

In other words, the catalytic activity for hydroxylation of benzene decreased with the number of vanadium centers in the polyoxoanion system. The catalyst activity data indicated that $PMo_{11}V$ was comparatively more active than di and tri vanadium substituted catalysts. The decrease in the catalytic activity of the di and tri vanadium substituted catalysts could be due to the poor stabilities of the corresponding peroxo intermediate species in the oxygen transfer reaction. Fig.1 shows the conversion of benzene with the number of vanadium centers in the heteropolyacid.

Fig.1 Time course of benzene hydroxylation with hydrogen peroxide catalyzed at 338 K in acetonitrile. (a)o, PMo11V; (b) ð, $PMo_{10}V_2$; (c) •, PMo_9V_3



5.3.2 Kinetics of hydroxylation of benzene to phenol catalyzed by $PMo_{11}V$

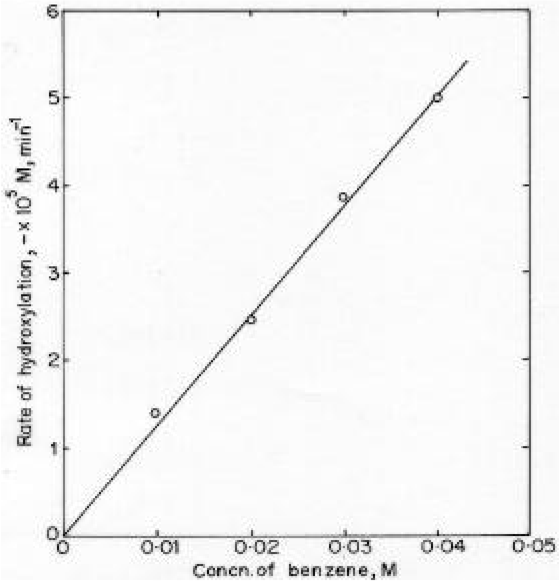
Hydroxylation of benzene catalyzed by $PMo_{11}V$ under the given reaction conditions yielded phenol. Hence, kinetic investigations of this reaction were carried out to establish the dependence of rate of hydroxylation with respect to the variations in the concentrations of the reactants involved in the system in excess acetonitrile solvent. The total volume of the reaction mixture in all kinetic experiments was adjusted to 10 mL by the addition of acetonitrile solvent. Rates of hydroxylation of benzene were calculated from the plots of moles of benzene reacted vs. time.

The reaction parameters were varied to determine the rate of the reaction.

(a) Effect of substrate concentration

Experiments on hydroxylation of benzene were carried out at 338 K by varying the concentrations of the substrate benzene as 0.01,0.02,0.03 and 0.04 M, while keeping the concentrations of H_2O_2 (0.02M) and catalyst (2.33 x 10^{-5}M) constant. The effect of substrate concentration on the rate of hydroxylation of benzene is shown in Fig.2 , as a plot of rate *vs.* concentration of benzene.

Fig 2 Effect of benzene concentration on the rate of hydroxylation

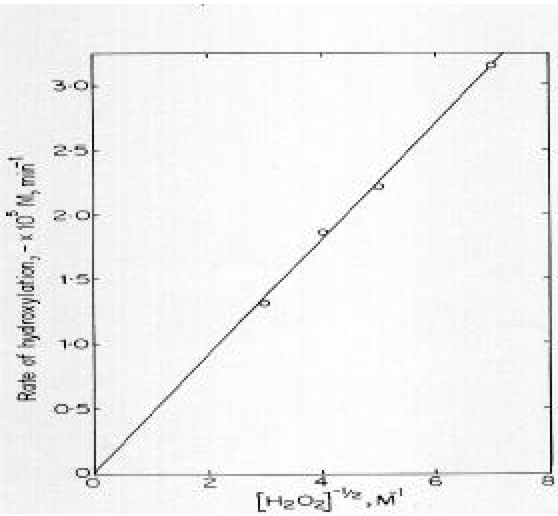


It was found that the rate of hydroxylation of benzene to phenol showed a first order dependence with respect to substrate concentration.

(b) Effect of H_2O_2 (oxidant) concentration

Keeping substrate as 0.02 M, catalyst, 2.33 x 10^{-5} M and temperature, 338 K constant, the H_2O_2 concentration was kept as 0.02, 0.04, 0.06 and 0.1 M. The graph of rate of hydroxylation vs. $[H_2O_2]^{1/2}$ is given in Fig.3.

Fig.3 Effect of oxidant concentration on rate of hydroxylation

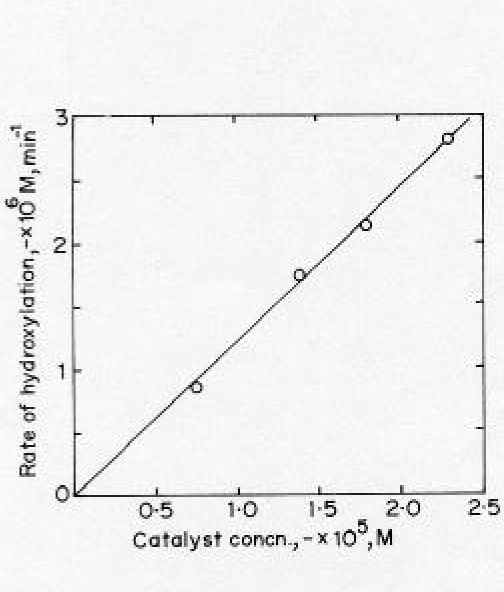


The graph is linear and showed a half-order dependence with respect to oxidant concentration. In other words, half a mole of oxygen is transferred from oxidant to benzene to give phenol.

(c) Effect of catalyst concentration

Catalyst concentration was kept as 0.75 x 10^{-5}, 1.4 x 10^{-5}, 1.86 x 10^{-5} and 2.33 x 10^{-5} M, at substrate, 0.02 M, oxidant, 0.1 M and temperature 338 K. Fig.4 shows the graph of rate of hydroxylation vs. catalyst concentration .

Fig.4 Effect of catalyst concentration on rate of hydroxylation

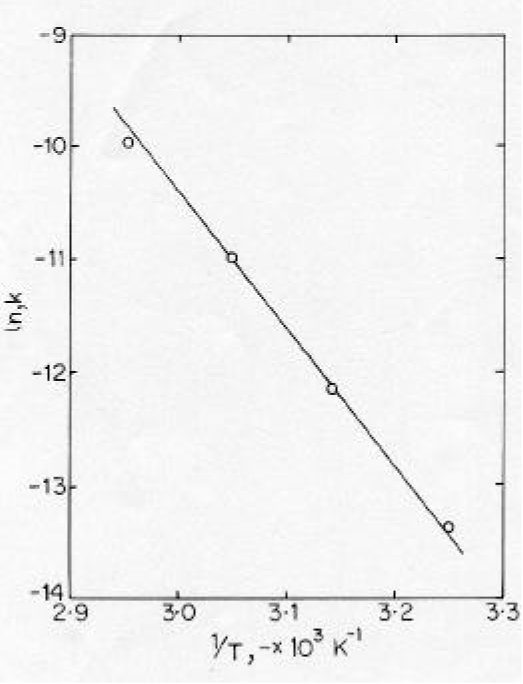


It is seen from the graph that the rate of hydroxylation has a linear and first order dependence with respect to catalyst concentration.

(d) Effect of temperature

Effect of temperature on the rate of hydroxylation of benzene to phenol was studied by varying the temperature as 308, 318, 328 and 338 K, while other parameters were kept constant as substrate, 0.02 M, oxidant, 0.02 M and catalyst, 2.33 x 10^{-5} M. From Arrhenius plot of ln k *vs.* 1/T shown in Fig.5, the activation energy E_a evaluated was 21.5 kcal $mole^{-1}$.

Fig.5 Arrhenius plot

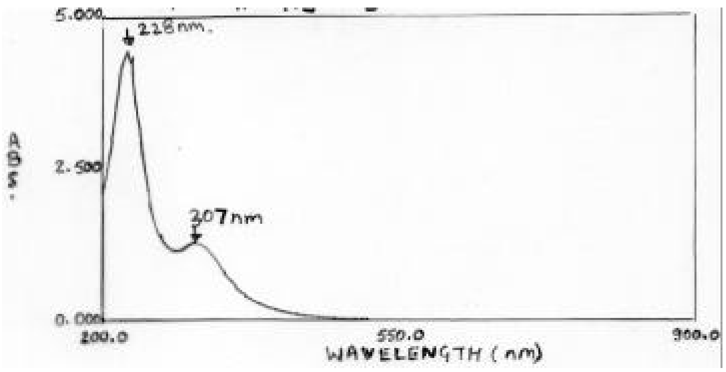


In order to understand the transient species formed during the course of the above reaction, the reaction mixtures were subjected to UV-Visible and EPR spectroscopic studies at regular time intervals.

5.3.3 UV-Visible spectroscopy

The UV-Visible spectra of the neat catalyst $PMo_{11}V$ in acetonitrile showed absorption maximum at 307 nm as shown in Fig.6. This band at 307 nm is associated with octahedrally coordinated Mo^{6+} and arises due to ligand to metal charge transition [14]. The presence of vanadium in the Keggin structure has broadened the LMCT band.

Fig. 6 Electronic spectra of the catalyst $PMo_{11}V$ in acetonitrile



The study of the relative change in catalyst with the reaction was done by subjecting the reaction mixture to spectroscopic techniques like electronic and electron spin resonance spectroscopy. A fixed amount of the reaction mixture containing the substrate, oxidant, catalyst and the solvent was taken for the above mentioned spectroscopic techniques.

A fixed volume (0.075 gm) of the reaction mixture diluted with acetonitrile to 10 ml in a volumetric flask was exposed to absorption spectroscopy at regular time interval of 30 minutes. Upon the addition of the oxidant and substrate to the catalyst solution, the UV-Visible spectra showed the appearance of a new band at 330 nm in addition to the already existing band at 307 nm. This new band at 330 nm could be due to the formation of vanadium (V) peroxo species, which is an active intermediate, formed as a result of interaction of the vanadium center with hydrogen peroxide. The intensity of this band increased linearly during the course of the reaction. This increase in intensity is an indication of phenol formation and simultaneous H_2O_2 decomposition in the system. The intensity was found to reduce as the concentration of phenol remained constant in the course of the reaction. This was verified by gas chromatographic analysis. Fig.7 shows the UV-Visible spectral changes for the reaction mixture containing $PMo_{11}V$, $PMo_{10}V_2$ and PMo_9V_3. Similar pattern was observed, when the di and tri vanadium substituted catalysts were used. Active intermediate species were formed in all the three catalysts but their stabilities were found to be different. The active species formed by mono vanadium substituted phosphomolybdic acid was more stable than the other two. This observation supported the fact that only a single vanadium site ($PMo_{11}V$) is needed for hydroxylation reaction .

Fig.7 (a) Absorption spectra of $PMo_{11}V$ as a function of time

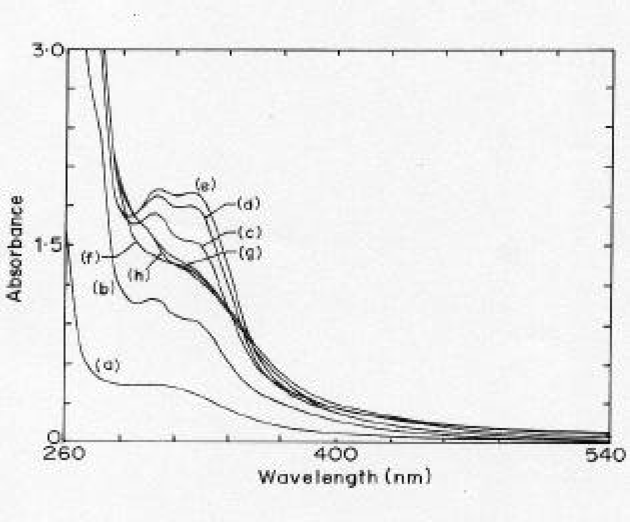


Fig.7(b) Absorption spectra of $PMo_{10}V_2$ as a function of time

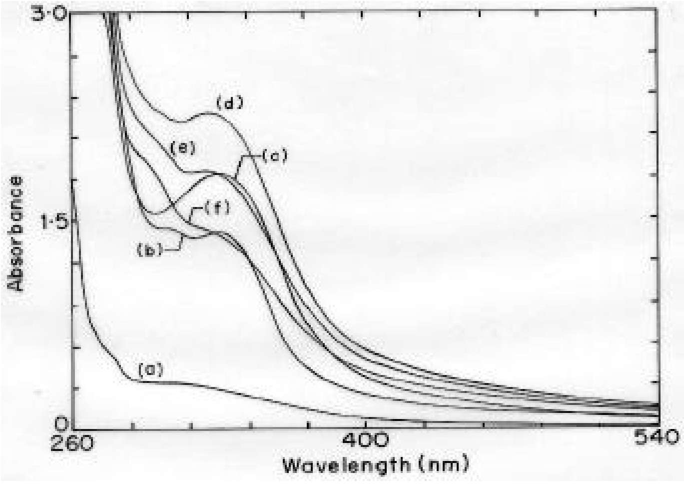
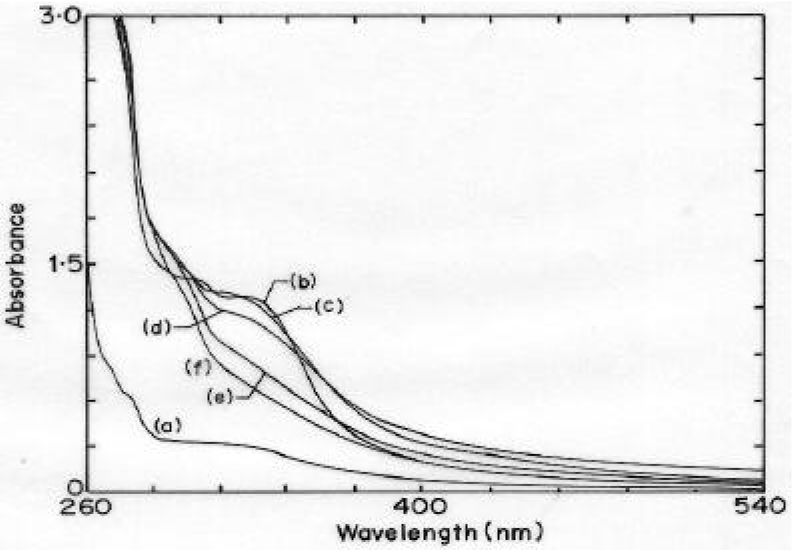


Fig 7(c) Absorption spectra of PMo_9V_3 as a function of time



5.3.4 EPR spectroscopy

Vanadium substituted heteropolymolybdates $PMo_{11}V$, $PMo_{10}V_2$ and PMo_9V_3 showed EPR spectra typical of a vanadium (IV) ion [15]. The spectra of solid samples were broad due to spin-spin interactions. The CH_3CN solution spectra showed eight narrow signals (H_{pp}= 12 G). These signals arose due to the interaction of unpaired electron spin (S =1/2) with the nuclear spin of vanadium (^{51}V has a nuclear spin I = 7/2 with a natural abundance of 99.75 %). The separation between the adjacent hyperfine signals is not equal due to second order interactions and increases from 105 G to 129.5 G in increasing field direction. The isotropic g and hyperfine coupling constants were estimated to be 1.965 and 117 G, respectively. The spectra for frozen CH_3CN solutions, at 77 K, were almost similar for all the three vanadium containing catalysts and were characterised by an axial g and hyperfine tensors ($g = 1.933$, $g_{\perp} = 1.977$, $A = 202.0$ G and $A_{\perp} = 76.7$ G). $PMo_{10}V_2$ and PMo_9V_3 samples did not reveal the presence of multinuclear vanadium centres.

Inspite of vanadium being in the +5 oxidation state in the source of vanadium used for synthesis the samples were found to be paramagnetic and showed EPR signals corresponding to the +4 oxidation state of vanadium. The V^{4+} species may be formed during the synthesis stage of the these catalysts. These results, therefore, suggest that a small quantity of vanadium is probably present as VO^{2+} ion outside the Keggin structure compensating for two H^+ ions. Bayer *et al* have reported the formation of $(VO)^{2+}H_2[PMo_{11}V]$ during the synthesis of $PMo_{11}V$ [16]. In our samples the former type is probably present at impurity levels. EPR spectroscopy being a sensitive technique for paramagnetic ions has detected these impurity species. Vanadium substituted for molybdenum ions in the Keggin structure, is in +5 oxidation state.

EPR spectroscopy is used to monitor the paramagnetic transient species formed during benzene hydroxylation by vanadium substituted heteropolymolybdates. This technique revealed the role of vanadium in the catalytic hydroxylation of benzene. A known amount of the sample was taken out each time from the reaction mixture at specified times and spectra were recorded after quenching the samples to 298 and 77 K, respectively. Spectra for the reaction mixture containing the catalyst $PMo_{11}V$, $PMo_{10}V_2$ and PMo_9V_3 at different reaction times is shown in Fig.8(i), 8(ii) and 8(iii) respectively. The spectral variations for all the three catalysts are, in general, similar.

Fig.8 (i) Room temperature EPR spectra of $PMo_{11}V$ in the reaction mixture as a function of time: (a) $PMo_{11}V$+ benzene +CH_3CN, (b) reaction mixture + H_2O_2 at 0 min, (c) 90 min, (d) 24 h. Species II is maximum at 90 min.

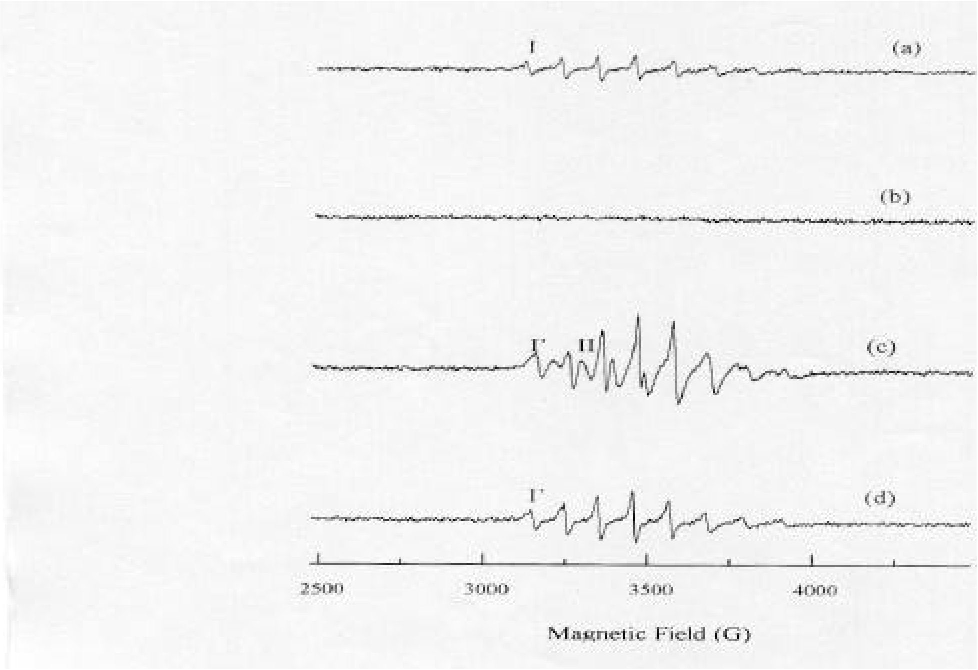


Fig.8 (ii) Room temperature EPR spectra of $PMo_{10}V2$ in the reaction mixture as a function of time: (a) $PMo_{11}V$+ benzene +CH_3CN, (b) reaction mixture + H_2O_2 at 0 min, (c) 60 min, (d) 90 min, and (e) 24 h. Species II is maximum at 60 min.

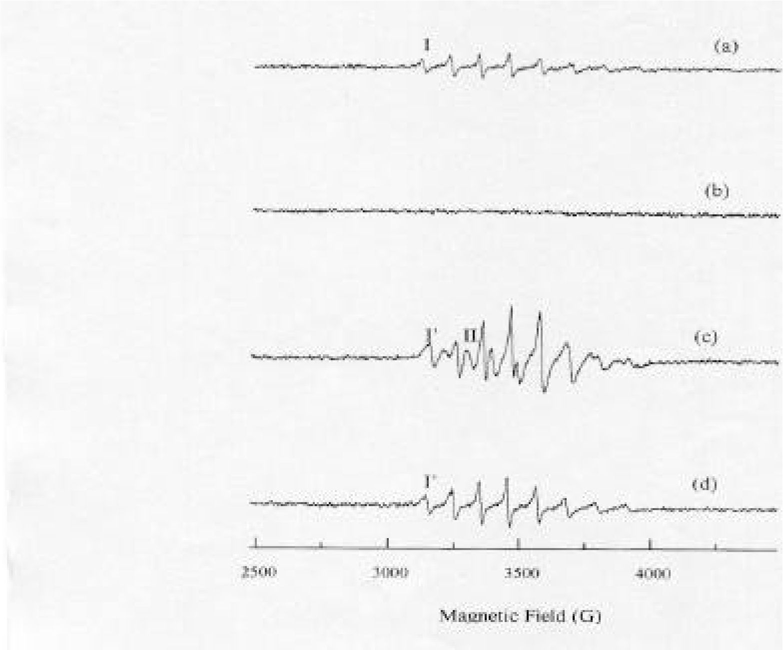
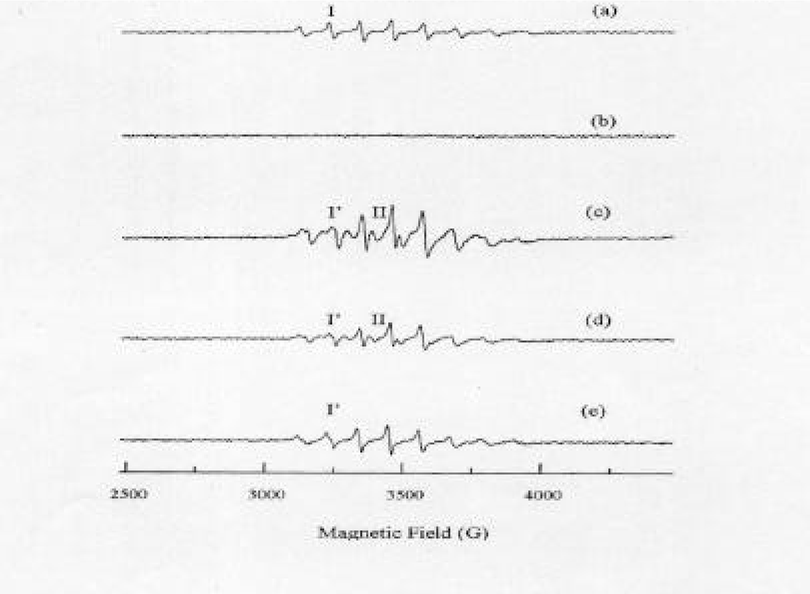


Fig.8 (iii) Room temperature EPR spectra of PMo_9V3 in the reaction mixture as a function of time:
(a) PMo_9V_3+ benzene +CH_3CN, (b) reaction mixture + H_2O_2 at 0 min, (c) 30 min, (d) 90 min and (e) 24 h. Species II is maximum at 30 min.



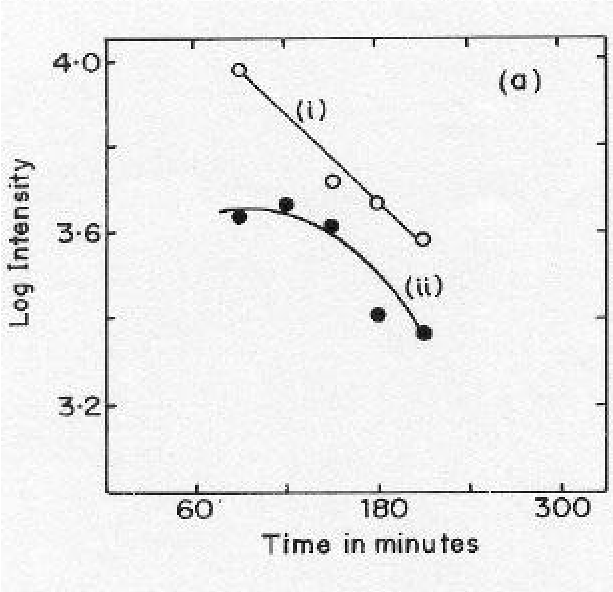
The CH_3CN solutions without H_2O_2 are paramagnetic due to trace quantities of VO^{2+} as the counter cation [species I; Fig.8(i)(a)]. Soon after adding H_2O_2, the solutions became EPR silent due to the oxidation of V(IV) to V(V) [Fig.8(i)(b)]. After a certain time, signals corresponding to two new vanadium(IV) species I' and II appeared [Fig.8(i)(c)] . The Hamiltonian parameters of these species are different (g_{iso}=1.970, A_{iso}=108.2 G for species I' and g_{iso}= 1.963 and A_{iso}= 95.2 G for species II) from those of original species I (g_{iso}= 1.965 and A_{iso}= 117.0 G). A lower value for A_{iso}, especially for species II reveals lower symmetry at the site of vanadium and higher delocalization of electron density onto the ligands. The intensity of the signals for species I’ and II was maximum at a reaction time of 90 minutes for $PMo_{11}V$, 60 minutes for $PMo_{10}V_2$ and 30 minutes for PMo_9V_3 catalyst systems and then onwards, signals of species II decreased and finally disappeared as shown in Fig. [8(i)(d)].

Variation of log intensities of signals for species I’ and II for all the three catalysts are shown in Fig. 10.

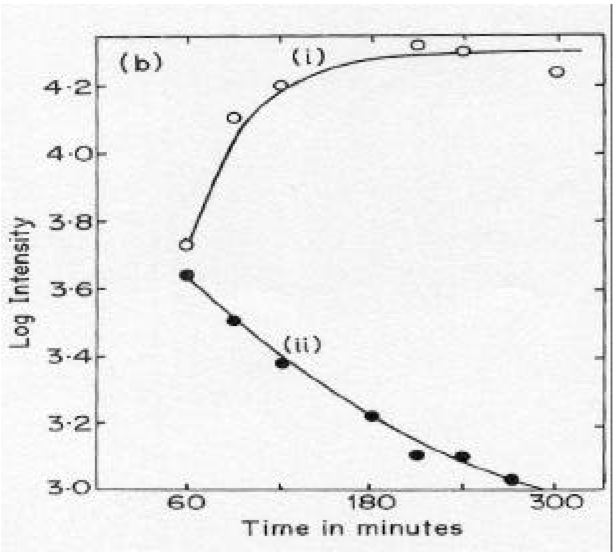
Fig. 9 Plot showing the variation of EPR signal intensity for species I’ (I) and species II

(ii) as a function of time.

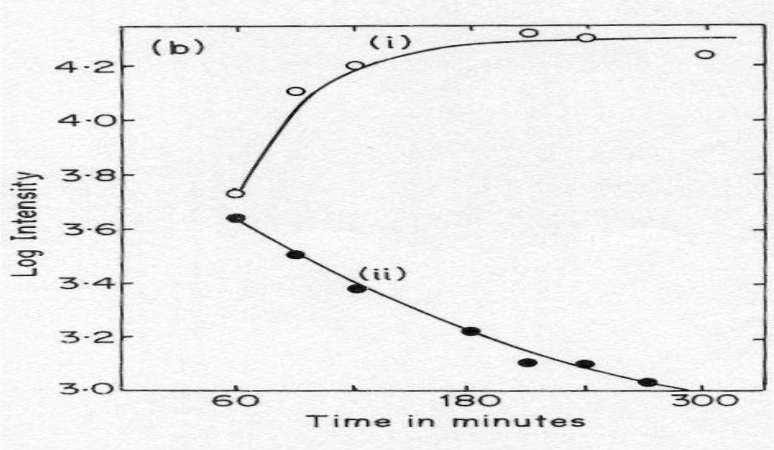
(a) $PMo_{11}V$



(b) $PMo_{10}V_2$



(c) PMo_9V_3

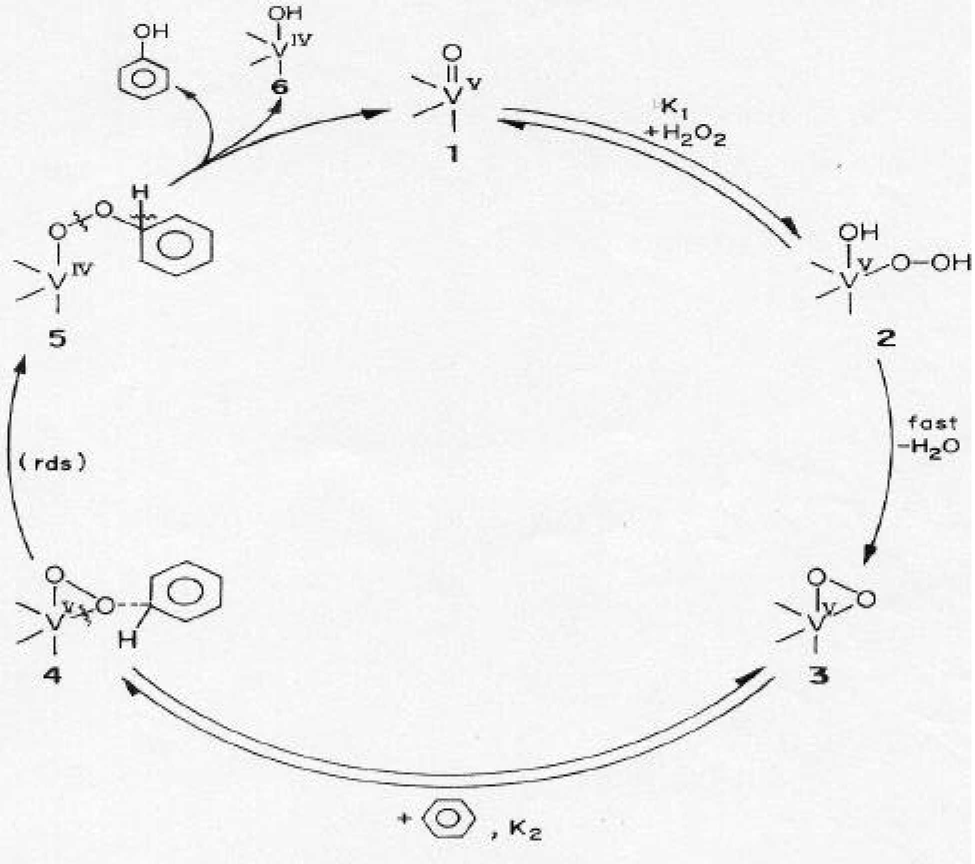


While the behaviour of intensity variation is similar for $PMo_{10}V_2$ and PMo_9V_3 this variation for the catalyst system $PMo_{11}V$ is different, especially for species I'. This signal intensity of species I' for $PMo_{10}V_2$ and PMo_9V_3 increased gradually and reached a maximum value while that for $PMo_{11}V$ decreased with time. The spectra after 24 h contained signals due to species I'only (Fig.3(d)). The overall spectral intensity of the vanadium (IV) ion increased at the end of the reaction and suggests that a part of the substituted vanadium leaches out during the course of the reaction. This leaching for catalysts $PMo_{10}V_2$ and PMo_9V_3 is more and thus shows a different type of intensity variation for species I'. It is interesting to note that molybdenum centre is not involved in the hydroxylation reaction.

5.3.5 Mechanism and rate law

Based on the spectroscopic and kinetic observations made in the system, a mechanism has been proposed for vanadium substituted heteropoly acid catalyzed hydroxylation of benzene to phenol and is shown in Fig 10.

Fig.10 Reaction mechanism for the hydroxylation of benzene



The proposed mechanism involves the transformation of vanadium in heteropolymolybdates to an unstable vanadium (V) hydroxy hydroperoxy species **2,** on interaction with hydrogen peroxide in a pre-equilibrium step. Species **2,** rapidly transforms into a relatively stabler vanadium (V) peroxo species **3** on loss of a water molecule. This species has been identified and shows a band at 330 nm in the UV-Visible spectra. The species **3,** interacts with the substrate benzene in another pre-equilibrium step to give a metallo- peroxy-arene intermediate species **4**. Transfer of oxygen by C-H bond activation takes place in a rate determining step (rds) to give vanadium (IV) phenoxy intermediate species **5**. The species **5** has been identified as species II in the EPR spectrum (Fig.3(c)). Homolytic cleavage in species **5** results in rapid dissociation to give phenol and regenerating the species **1** and a small amount of vanadium (IV) hydroxo species **6**, in a catalytic cycle. Species **6** has been identified as a stable species I' in the EPR spectrum. The built in concentration of inactive species **6** reduced the catalytic activity in the system.

Based on the reaction mechanism and kinetic rate dependence studies, the rate law for $PMo_{11}V$ catalyzed hydroxylation of benzene to phenol could be written as:

$$\text{rate} = kK_1K_2\,[\text{HPA-V}][S][H_2O_2]^{1/2} \qquad (1)$$

Where, k = over all rate constant of the reaction, K_1 and K_2 are, pre-equilibrium constants as shown in Scheme-I, [HPA-V] = $PMo_{11}V$ catalyst conc., [S] = benzene concn. and $[H_2O_2]$ = hydrogen peroxide conc., respectively.

By applying steady state reaction conditions and the total concentration of catalyst present in different forms (shown in Scheme-I) is expressed as $[\text{HPA-V}]_T$, then the rate law can be modified as:

$$\text{rate} = \frac{kK_1K_2\,[\text{HPA-V}]_T[S][H_2O_2]^{½}}{1 + K_1\,[H_2O_2]^{1/2} + K_1K_2[S][H_2O_2]^{1/2}} \qquad (2)$$

To evaluate equilibrium and kinetic constants graphically, eqn. 2, could be rearranged in a slope and intercept form in the following two ways as:

$$\boldsymbol{\frac{[\text{HPA-V}]_T}{\text{rate}} = \frac{1}{[S]}\left(\frac{1}{kK_1K_2[H_2O_2]^{1/2}} + \frac{1}{kK_2}\right) + \frac{1}{k}} \qquad \textbf{(3)}$$

$$\frac{[\text{HPA-V}]_T}{\text{rate}} = \frac{1}{[H_2O_2]^{1/2}}\left(\frac{1}{kK_1K_2\,[S]}\right) + \frac{1}{k}\left(1 + \frac{1}{K_2[S]}\right) \qquad (4)$$

From eqn.3, a plot of $[HPA\text{-}V]_T$/ rate vs. 1/[S] gives a straight line with an intercept from which, the value of k was calculated. Similarly from eqn.4, a plot of $[HPA\text{-}V]_T$/ rate vs. $1/[H_2O_2]^{1/2}$ gives a straight line and substituting the value of k, in the slope and intercept values of this graph, the pre-equilibrium constants K_1 and K_2 were obtained. Thus, the values of k, K_1, K_2 for the hydroxylation of benzene to phenol catalyzed by $PMo_{11}V$ at 338 K were found to be as k = 8.33, min^{-1}, K_1 = 39.4, M^{-1} and K_2 = 2.63, M^{-1}, respectively.

From the temperature dependence study carried out on hydroxylation of benzene to phenol, the energy of activation was evaluated. Other thermodynamic activation parameters, such as, enthalpy of activation ($H^{\#}$), entropy of activation ($S^{\#}$) and free energy of activation ($G^{\#}$) were calculated from standard thermodynamic equations. These values are, Ea = 21.5 kcal mol^{-1}, $\Delta H^{\#}$ = 20.9 kcal mol^{-1}, $\Delta S^{\#}$ = 48.1 cal deg^{-1} mol^{-1} and $\Delta G^{\#}$ = + 5.37 kcal mol^{-1}.

5.4. Summary

The catalytic activities of vanadium containing heteropolymolybdates of the general formula $H_{3+x}[PMo_{12-x}V_xO_{40}]$. n H_2O where, x = 1,2,3 in the selective hydroxylation of benzene were investigated using hydrogen peroxide as oxidant. GC analysis revealed phenol as the only product of oxidation. The effects of various parameters like temperature, the concentrations of substrate, catalyst and oxidant on the rate of hydroxylation of benzene were studied and thermodynamic activation parameters were estimated. The UV-Visible and EPR spectroscopic techniques were used to monitor the active intermediate species. A mechanism of hydroxylation reaction involving vanadium (V) peroxo intermediate species has been proposed. It is seen that the mono vanadium substituted phosphomolybdate is the most active for the oxidation of benzene to phenol compared to the di and tri vanadium substituted acids.

5.5 References

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CHAPTER – 6

CYCLOHEXANE OXIDATION

6.0 Cyclohexane oxidation

6.1 Introduction

6.2 Experimental

6.3 Results and Discussion

6.4 Conclusions

6.5 References

6.1 Introduction

Transformation of hydrocarbons into oxygenated products has been extensively investigated over the past many years as such products are valuable intermediates for organic synthesis in the laboratory as well as in the industry. In the bulk chemical industry, classical processes are environmentally unacceptable, non-selective and thus have been largely supplanted by cleaner catalytic alternatives. Among hydrocarbons, the oxygenation of alkanes has attracted much attention because they are abundant as resources and

low in reactivities as feedstocks. In this chapter we shall discuss the oxidation of the hydrocarbon, cyclohexane in detail. The partial oxygenated products of cyclohexane are valuable precursors for industrial chemicals. The liquid phase aerial oxidation of cyclohexane to cyclohexanol and cyclohexanone was developed in 1940s. The oxidation of cyclohexane is usually carried out with a soluble cobaltnaphthate catalyst in a series of stirred autoclaves at 140-180°C at 0.8-2 MPa of air. The initial oxidation product is cyclohexyl hydroperoxide, which is converted into to cyclohexanol and cyclohexanone (2:1 molar ratio) and the reaction is as shown below:

$$C_6H_{12} + O_2 \text{ -----> } C_6H_{11}OOH \quad (1)$$

$$3C_6H_{11}OOH \text{ ----> } 2C_6H_{11}OH + C_6H_{10}O + H_2O + O_2 \quad (2)$$

Because these products are more readily oxidized than cyclohexane, conversion must be kept low (<10 %) in order to maximize yield of alcohol and ketone, respectively. The current challenge involves the study the metal complexes catalyzed oxidation of cyclohexane with high selectivity towards oxygenated products. With respect to the oxidants, fine chemical production allows the choice of various oxygen donors such as peroxides. Among them hydrogen peroxide is a preferable oxidant due to its simplicity in handling, environmentally friendly nature of the co-product i.e. water, high percentage of active oxygen (47%) and its versatility in the oxidation reactions. In this context the development of efficient catalyst for the oxidation of hydrocarbons is very attractive and challenging. The current challenge involves the study the metal complexes catalyzed oxidation of cyclohexane with high selectivity towards oxygenated products. Heteropolycompounds, especially those with Keggin-type structure have created a renewed interest in the oxidation of organic substrates under homogenous and heterogeneous reaction conditions. The advantages of heteropoly compounds as catalysts are: (a) Thermal and chemical stability, (b) Wide range of possibilities for modifying the Keggin structure without affecting its primary structure, (c) Reactivity with a wide range of oxygen donors like hydrogen peroxide, tert-butyl hydrogen peroxide, iodosylbenzene, persulphate, molecular oxygen, etc. and (d) High resistance to oxidative degradation. These properties of heteropoly compounds lead to their valuable application in catalysis. Cyclohexane oxidation under mild reaction condition has been successfully carried out with many transition metal substituted polyoxometalates. Most of the literature reports include the use of Co^{2+}, Fe^{3+}, Cr^{3+}, Ru^{3+} and Rh^{3+} substituted polyoxotungstate as catalysts using either H_2O_2 or TBHP as oxygen donors [1-3]. The vanadium-substituted heteropolymolybdates have attracted attention as catalysts for many oxidation reactions. The reactivity of vanadium substituted phosphomolybdates towards oxygen donors like hydrogen peroxide is a subject of recent investigation [4-7]. The high reactivity of this system encouraged us to extend it to the family of saturated hydrocarbons, like methyl cyclohexane, naphthalene, and 1-methyl naphthalene and biphenyl substrates.

6.2 Experimental

6.2.1 Materials

Disodium hydrogen phosphate dodecahydrate, sodium molybdate dihydrate and sodium meta vanadate (all from M/s Loba Chemicals, Mumbai), conc.H_2SO_4 and diethyl ether were used as received for the preparation of molybdovanadophosphoric acid. Cyclohexane (M/s. S.D.Fine-chem.Ltd, Mumbai), aqueous 30%H_2O_2 (M/s. E.Merck India Ltd, Mumbai) and acetonitrile of high purity were used without further purification. The exact strength of hydrogen peroxide was determined by redox titration against standard $KMnO_4$. The catalysts were prepared by methods described in chapter 2.

6.2.2 Procedure

Procedure for the determination of strength of hydrogen peroxide

The peroxide content in the commercially available hydrogen peroxide is determined by the procedure described in chapter 5.

Procedure for catalytic run

The liquid phase oxidation reactions were carried out in a two necked 50 ml round bottom flask immersed in a thermostated oil bath maintained at 65°C. A typical reaction mixture included 0.05g (0.025 mmol) of catalyst, 1.68g (20 mmol) of cyclohexane, 2.36 (20 mmol) of aqueous hydrogen peroxide and 20 ml acetonitrile. A magnetic stirrer was provided to stir the reaction mixture. The reaction mixture was subjected to GC analysis for product estimation. The samples were analyzed simultaneously by ^{51}V and ^{13}C NMR spectroscopy at regular time intervals of 30 minutes to identify the active intermediate species. Similarly 0.02 M of substrates like methyl cyclohexane, naphthalene, 1-methyl naphthalene and biphenyl were taken in 20, 5, 5 and 8 gm acetonitrile respectively, and oxygenated under the same reaction conditions as cyclohexane.

Analysis of products: The liquid products of cyclohexane and methyl cyclohexane oxidation were analyzed by gas chromatography on a Shimadzu GC-14B equipped with a 2 meter, 10 % carbowax 1560 with diameter 1/8" and having a flame ionization detector.The other substrates were analyzed on Shimadzu GC-14B using a HP-5 fused column with 30m x 0.53mx 1.5 μm film thickness and F.I.D detector.*In situ* nuclear magnetic resonance spectroscopy was done by withdrawing the cyclohexane reaction mixture at regular intervals of 30 minutes. The ^{51}V and ^{13}C NMR spectra were recorded on a Bruker instrument MSL 300. The measurements were carried out at 75.47 MHz for ^{13}C and 78.9 MHz for ^{51}V using a standard 10 mm probe. An external D_2O lock was used for all the measurements. The chemical shifts for ^{51}V used $VOCl_3$ as the external standard while for ^{13}C the standard is dioxane in D_2O.

6.3 Results and discussion

6.3.1 Catalyst characterisation

The molybdovanadophosphoric acids of the kind $H_4[PMo_{11}VO_{40}]$. nH_2O, $H_5[PMo_{10}V_2O_{40}]$ $.nH_2O$ and $H_6[PMo_9V_3O_{40}]$ $.nH_2O$ were characterised by thermal analysis, FTIR, UV- Visible and atomic absorption spectroscopy as described in chapter 5. *Insitu* ^{51}V and ^{13}C NMR spectroscopy was carried out to establish the reaction mechanism for cyclohexane oxidation.

6.3.2 Catalytic activity

After benzene hydroxylation the catalytic activity of the mono, di and tri vanadium substituted phosphomolybdic acids was extended to saturated substrates like cyclohexane with H_2O_2 as the source of oxygen. The reaction conditions and the results are presented in table 1.

Table 1. Catalytic activities in oxidation of cyclohexane

Catalyst system	Cyclohexane Conv.(Wt.%)	Selectivity, (Wt.%)		TON^a
		Cyclohexanol	Cyclohexanone	
$H_4[PMo_{11}VO_{40}]$	15.9	66.2	33.8	147.4
$H_5[PMo_{10}V_2O_{40}]$	13.5	61.2	38.8	108.8
$H_6[PMo_9V_3O_{40}]$	12.2	59.9	40.1	97.3

Conditions: Cyclohexane (0.02 M), H_2O_2 (0.02 M), Catalyst (0.025 mM), Acetonitrile (20 ml),Temperature (65°C), Reaction time (2h) and
TON^a = Turnover number (mol substrate consumed per mol catalyst).

From the results presented in Table 1, it is evident that $H_4[PMo_{11}VO_{40}]$ is the best performed catalyst in the oxidation of cyclohexane and hence, we tested this catalyst for its activities in the oxidation of substituted benzenes such as methyl cyclohexane, naphthalene, 1-methyl naphthalene and biphenyl and the results are presented in Table 2.

Table 2
Activity of $H_4[PMo_{11}VO_{40}]$ in the oxidation of aromatic hydrocarbons

Substrate	Convn.(%)	TON^a	Products (%, Selectivity)
Methyl cyclohexane (in 20 g CH_3CN)	0.9	9.2	Methyl cyclohexanone (38.0) Methyl cyclohexanol (58.0) Others (4.0)
Naphthalene (in 5 g CH_3CN)	6.9	64.5	2, Naphthol (17.7) 1,4-Naphthoquinone (56.7) Phthalic anhydride (13.6) Others (12.0)
Biphenyl (in 8 g CH_3CN)	2.8	27.6	o-Hydroxy biphenyl (41.5) 2,5-Cyclohexadiene,1,4-Dione,-2-Phenyl (43.7) Others (14.8)
1-Methyl naphthalene (in 5 g CH_3CN)	4.0	41.5	2,Methyl-1,4-Naphthalene (62.6) 2,Methyl-1,Naphthol (30.8) Others (6.6)

Conditions: Substrate (0.02 M), H_2O_2 (0.02 M), Catalyst (0.025 mM), Temp (65°C), Time (1.0 h).
TON^a = Turnover number (mol substrate consumed per mol catalyst).

The oxidation of cyclohexane was followed by G.C analysis and NMR spectroscopy. Both ^{51}V and ^{13}C nuclei were used in the study. These techniques were used for the identification of an active intermediate species leading to the formation of products in the above oxidation reaction.

The molybdovanadophosphate-H_2O_2 system readily oxidizes cyclohexane in acetonitrile at 65° C to give cyclohexanol and cyclohexanone. Triphenylphosphine (PPh_3) was added to the reaction products and the GC analysis of this showed a sharp increase in the concentration of cyclohexanol, while the concentration of cyclohexanone substantially reduced. This proves that cyclohexane oxidation proceeds via the cyclohexylhydroperoxide (intermediate) formation, which is found to be reduced by PPh_3. Cyclohexylhydroperoxide is short lived and gets decomposed in the chromatographic column to yield the corresponding alcohol and ketone.

Spectroscopic evidence

^{51}V NMR spectroscopy

The catalysts used for investigating the reaction mechanism was $H_4[PMo_{11}VO_{40}]$. nH_2O. The ^{51}V NMR spectra of the above catalysts was taken in acetonitrile. The spectrum exhibited a single peak at – 560.41 ppm typical for a mono vanadium substituted phosphomolybdic acid as shown in figure1. Hydrogen peroxide was then added to the above solution and the mixture refluxed for half an hour. The solution was then subjected to ^{51}V NMR spectroscopy. This spectrum showed two peaks one at – 543.4 ppm and the other at – 641.9 ppm as seen in figure 2. The former is due to the catalyst while the latter may be assigned to the formation of $H_4[PMo_{11}VO_{40}]$ - peroxo compound generated in solution

^{13}C NMR spectroscopy

Oxidation reaction was followed by ^{13}C NMR (natural abundance) spectroscopy at different intervals of time. The ^{13}C NMR spectra of the reaction mixture exhibited peaks due the formation of reaction intermediates and products (Fig.3). Peaks are observed at 210, 85, 71, 36.96, 31.91, 27.19, 25.87 and 25.32 apart from the signals arising from acetonitrile (2.3 ppm, 119 ppm) and cyclohexane (28 ppm). The signals at 85, 31.91, 27.19,25.32 ppm are assigned to the cyclohexyl hydroperoxide formed during the reaction [10]. Resonance peaks at 71, 36.96, 25.87 ppm are due to the different carbons of cyclohexanol, which is the major product formed. The peaks at 210, 43, 25.87 ppm are arising from cyclohexanone formed in the reaction medium.

The ^{13}C spectra were also taken after the addition of triphenyl phosphine in the reaction mixture (Fig.4). The spectrum showed a considerable decrease in the intensities of the peaks arising from cyclohexanone. For example, the carbonyl peak at ~ 210 ppm was reduced almost to noise level. This clearly indicates that the formation of cyclohexanone is supressed in the reaction while cyclohexanol is found to predominantly exsist in the reaction mixture. There is a decrease in the intensity of the signal at 33.96 and 25 ppm. The disappearance of peaks at 85 ppm indicates that the cyclohexyl hydroperoxide formed during the reaction has been reduced by the added triphenylphosphine. This goes in accordance with the GC result that the oxidation reaction proceeds through cyclohexyl hydroperoxide formation before the final products of oxidation are formed.

Mechanism

The ^{51}V NMR spectra of the catalyst was taken in acetonitrile, which exhibited a single resonance at –560.41 ppm (Fig. 3 a) The formation of species **IV** has been confirmed by taking the ^{51}V spectrum of the catalyst in the presence of hydrogen peroxide without substrate under identical conditions, which showed signals at –545 ppm and –648 ppm. The resonance at –527.36 ppm may correspond to similar vanadium (V) species along with the oxidation reaction. After a contact time of 1 h, a signal at –637.43 ppm (Fig. 3 c) appeared, which could be due to other similar species of vanadium-peroxo having a different chemical environment. Vanadium peroxo species **IV** rapidly undergo one electron reduction by the loss of one electron to form V^{IV}

6.4 Conclusions

In this chapter we continued the description of molybdovanadophosphates as catalysts for cyclohexane oxidation in acetonitrile medium with hydrogen peroxide as oxidant under homogeneous reaction conditions. Oxidation with higher selectivity towards cyclohexanol has been achieved and a comparison of the efficiency of mono-, di- and tri-vanadium substituted catalysts has been carried out. The reaction mechanism was established by performing *in situ* ^{51}V and ^{13}C NMR spectroscopy and confirmed that cyclohexyl hydroperoxide is the active reaction intermediate. The oxidation study was extended to other types of hydrocarbons too.

6.5 References

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CHAPTER – 7

SYNTHESIS, SPECTRAL AND SINGLE CRYSTAL CHRACTERISATION OF TRIS TETRABUTYL AMMONIUM PHOSPHODODECAMOLYBDATE

7.0 SYNTHESIS, SPECTRAL AND SINGLE CRYSTAL CHARACTERISATION OF TRIS TETRABUTYL AMMONIUM PHOSPHODODECAMOLYBDATE

7.1 Introduction

Keggin type heteropoly compounds find usage in acid catalysis as they are stable in solution and solid form. Phosphomolybdic acid $H_3PMo_{12}O_{40}$ is a potential and promising solid acid catalyst for homogeneously catalysed reactions. In order to heterogenise the catalyst tetrabutyl ammonium salt is prepared and characterized.

The characterisation of tris tetrabutyl ammonium phosphododecamolybdate was carried out by techniques like CHN, T.G analysis, vibrational spectroscopy, electronic spectroscopy. The single crystal analysis was done by X-ray diffraction technique. The X-ray diffraction studies reveal that the compound has a Keggin like structure with tetrahedral PO_4 group at the center and MoO_6 octahedra forming a heteropolyanion with surrounding cationic groups.

7.2 Experimental

7.2.1 Materials

Phosphomolybdic acid and tetrabutyl ammonium bromide (both from Loba chemicals, India) were commercially available samples. Methanol used was Aldrich grade.

7.2.2 Procedure : Catalyst preparation

The tris tetrabutyl ammonium phosphododecamolybdate was prepared by adding excess solid tetrabutyl ammonium bromide to the aqueous solution of phosphomolybdic acid. The yellow precipitate that formed immediately was filtered and washed with cold water.

Single crystal preparation

The well defined prismatic crystals of the metal complex were obtained from a solution in methanol.

7.3 Results and discussion

Catalyst characterisation

Composition:

CHN and thermogravimetric analyses have been carried out to obtain the composition and thermal stability of the compound. CHN analysis results are in agreement with the composition $(TBA)_3\ PMo_{12}O_{40}$, the observed (calculated) values are C = 22.62% (22.6), H = 4.26% (4.24), N = 1.58% (1.65). TGA and DTG curves of the TBA salt are shown in Fig. 1. The total weight loss observed at 450 °C (~29%) is comparable to that expected for the composition $(TBA)_3\ PMo_{12}O_{40}$ (29.4%). The compound is stable up to 300 °C and a two-step weight loss is observed in the 300-450 °C temperature region. The first weight loss around 335 °C (~13%) corresponds to the loss of two n-butyl units from the tetrabutylammonium cation, $[(C_4H_9)_4N]_3PMo_{12}O_{40} \rightarrow [(C_4H_9)_2H_2N]_3PMo_{12}O_{40}$, and the second weight loss at 410°C corresponds to the complete decomposition of the compound. The two-step weight loss indicates relatively longer C-N bonds of two of the n-butyl groups of the n-butylammonium cation in the compound.

Vibrational spectra:

Infrared spectra of the TBA salt and the free acid are compared in Fig. 2. The four major bands observed at ~1060, ~960, ~880 and ~800 cm^{-1} in the spectrum of the free acid are due to ν_{as} P-O_a, ν_s Mo-O_d, ν_{as} Mo-O_b-Mo, and ν_{as} Mo-O_c-Mo vibrations, respectively. Because of the D_{2d} symmetry of the phosphate group in the free acid [1], only the ν_3 and ν_4 modes of vibrations of the phosphate group are observed at 1060 and 594 cm^{-1}. A comparison of the spectrum of the salt with that of the free acid indicates that the P-O stretching band at 1060 cm^{-1} is affected on salt formation and some additional bands also appear at lower frequencies. Observation of the additional vibrations in this region as well as the appearance of the ν_1 mode of vibration of the phosphate group at 955 cm^{-1} are indicative of the lowering of the symmetry of the phosphate group on salt formation. Additional vibrations are observed at 1107, 1031, 1010 and 980 cm^{-1} in the region of the ν_3 mode of vibration at 1060 cm^{-1}. Sanchez et al [2] have assigned the vibration at ~1030 cm^{-1} of polycrystalline $TBA_3PMo_{12}O_{40}$ as due to that of the cation. However, it is possible that the feature at 1031cm^{-1} in the spectrum is from the vibration of the phosphate group due to lowering of symmetry because of the following reasons, i) a very weak shoulder at ~1030 cm^{-1} is observed in the spectrum of the free acid, ii) Sanchez et al [2] have observed a very weak band at 1030 cm^{-1} in the spectra of $(NBu_4)_3$ $XMo_{12}O_{40}$ when X = P only and this band is not observed when X = Si, Ge or As (if this band were due to cationic vibrations, it would have been observed in all the cases), iii) in the case of simple inorganic phosphates, when the symmetry is lowered to C_s or C_1 (as in the case of $LaPO_4$), very weak bands are observed at 1025, 1010 and 980 cm^{-1} [3] as in the present spectrum. Single crystal studies have indicated that the phosphate group is of C_1 symmetry in the TBA salt (compared to the D_{2d} symmetry in the free acid) and therefore the prominent weak band at 1030 cm^{-1} observed in the spectrum of the TBA salt can be assigned to that of P-O vibration. The new band at 740 cm^{-1} in the spectrum of the TBA salt which was also observed in the spectra of X = P, Si, Ge and As in $(NBu_4)_3XMo_{12}O_{40}$ by Sanchez et al [2] may be assigned to cationic vibration.

Electronic spectra:

The electronic spectra of the free acid and the TBA salt are compared in Fig. 3. The spectral features are identical, two prominent bands are observed at 229 and 310 nm in the spectrum of the free acid as well as the TBA salt. So and Pope [4] have argued that the two charge transfer bands in the spectrum of the free acid are related to optical electronegativity difference between metal (Mo) and ligands (O). The two charge transfer bands are therefore due to a difference in the nature of the metal-ligand interaction and one of the charge transfer bands is due to the oxo-type oxygen in the MoO_6 octahedra. This is the shorter Mo-O bond in the MoO_6 octahedra and this oxygen is coordinated to only one Mo atom [1]. The identical spectral features of the free acid and the compound indicate that the Keggin structure is not much disturbed on the formation of the TBA salt.

X-ray Diffraction:

The well defined prismatic crystals of the metal complex were obtained by slow evaporation from a solution in methanol. X-ray data were collected on a PC controlled Enraf-Nonius CAD-4 single crystal X-ray diffractometer using MoK_α radiation (λ=0.70930 Å). The structure was solved by direct method using SHELXS-86[1]. The crystal belong to triclinic space group P-1 with the unit cell dimensions a = 14.182(2)Å ,b= 23.832(4) Å ,c = 26.355(5) Å and α = 96.40(1)°, β = 90.02(1)°, γ = 107.30(1)°. The volume is 8446(2) Å^3. It has a Keggin like structure with tetrahedral PO_4 group at the center and MoO6 octahedra forming a heteropoly anion which is surrounded by three tetrabutyl ammonium cations can be seen from the packing of the molecules (Fig-4.). The Keggin anion unit is shown in Fig 5. The structure was refined using SHELXL – 97 (2) which converged to a final R value of 0.0784 from 18407 observed reflections.

The electron-density peaks of the tetrabutyl ammonium cations were diffuse, showing high anisotropic vibration. Due to high thermal parameters of the butyl carbon atoms, hydrogen atoms were not included.

Crystal Structure of $C_{48}H_{108}Mo_{12}N_3O_{40}P$:

The tetrabutyl ammonium group has an extended conformation, with the thermal parameters increasing progressively along the chain. It is observed that some of the C-N distances in the tetrabutylammonium moiety are relatively larger (1.57(2)Å) compared to the other C-N distances (1.52 Å) as seen from Table-1. Thermogravimetric analysis showed a two step weight loss (Fig.1) in the range 300-450 °C. Around 335 °C two n-butyl units are lost which may be due to the observed difference in C-N bond distances.

Table-1. **Comparison of the C-N bond lengths in the tetrabutyl ammonium moiety**

Atom	A	B	C	D	E	F
N1 - C1	1.51(1)	1.51(2)	1.51(1)	1.53(1)	1.52(2)	1.52(2)
N1 - C5	1.51(2)	1.52(2)	1.53(1)	1.52(1)	1.53(2)	1.50(1)
N1 - C9	1.57(2)	1.57(1)	1.57(1)	1.55(1)	1.54(1)	1.57(2)
N1 - C13	1.55(1)	1.52(2)	1.52(1)	1.53(1)	1.54(2)	1.53(2)

7.4 Conclusions

The synthesis of the compound tris tetrabutyl ammonium phosphododecamolybdate was carried out and the single crystal isolated for X-ray diffraction study. The crystal belongs to triclinic space group. The crystal has a Keggin structure with tetrahedral PO_4 group at the center and the MoO_6 octahedra forming a heteropoly anion which is surrounded by three tetrabutyl ammonium cations. Other characterisation techniques such as IR, UV – Vis spectroscopy and thermal analysis have been used to confirm the formation of Keggin structure.

7.5 References

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CHAPTER –8

PHENOL HYDROXYLATION

8.0 Phenol Hydroxylation

8.1 Introduction

All the three dihydroxy derivatives of benzene are of great commercial importance. Catechol is the starting product for a series of important fine chemicals for pest control, pharmaceuticals, and flavours and aromas. The main uses of hydroquinone are as a photographic developer, polymerization inhibitor, and antioxidant. It is also an important intermediate for numerous dyes. Commercially important simple derivatives include the mono- and di-ethers of hydroquinone in particular, and the alkyl hydroquinones and their ethers. Resorcinol, the *meta*- isomer, which is in great demand, is not reported to be formed in the oxidation of phenol with hydrogen peroxide. The hydroxylation of phenol is a field of great challenge. The most widely used hydroxylating agent is hydrogen peroxide due to its environment friendly nature. Phenol hydroxylation has been widely investigated over various catalysts such as mineral acids, metal ions, metal complexes and supported metal oxides. Titanium silicalites such as TS-1, TS-2, Ti-beta, Ti-MCM-41, Ti-ZSM-48, TAPO-5, TAPO-11, VS-2, etc. [1] have also been reported for the hydroxylation of phenol, but all catalysts except TS-1 showed low catalytic activity or low product selectivity. The first commercial process utilizing TS-1 for the hydroxylation of phenol was introduced by Enichem. In Italy, Brichima runs a process for the hydroxylation of phenol with hydrogen peroxide in a 5000 ton-per-year plant in the presence of small amounts of iron- and cobalt-salt initiators; phenol is oxidized with 60% hydrogen peroxide at 40°C in a radical reaction [2]. The ratio of hydroquinone to catechol is between 40 : 60 and 20 : 80, with a total selectivity of over 90% and a phenol conversion of about 20%.The reaction temperature, solvent, molar ratio of phenol to hydrogen peroxide, reaction time, catalyst amount and method of hydrogen peroxide addition- all have been found to be the major factors affecting phenol conversion, hydrogen peroxide efficiency and product selectivity. Recently it has been reported by Feng-Shou Xiao that a novel complex oxide, hydrothermally synthesized in a Bi_2O_3-V_2O_5-CuO-H_2O system is catalytically active for phenol hydroxylation using hydrogen peroxide. The results obtained were comparable to those obtained when TS-1 was used as the catalyst, but the selectivity was more towards catechol than hydroquinone, the former being the more desired product. The new catalyst had a lower surface area than TS-1 and hence showed a much larger TON, a much longer catalyst life than TS-1., cheaper and efficient recyclability [3]. In another recent paper Feng-Shou Xiao describes a novel catalyst, copper hydroxyphosphate, $Cu_2(OH)PO_4$, as a better catalyst for the hydroxylation of phenol [4]. Comparative studies suggest that the unusual catalytic activity of this copper catalyst may be related to the unique structure of hydrothermally synthesized $Cu_2(OH)PO_4$.

The mono-vanadium substituted phosphomolybdic anion, mentioned in Chapter 5, is capable of hydroxylating benzene, and this work has been extended to hydroxylation of phenol in this chapter.

8.2 Experimental

8.2.1 Materials

Disodium hydrogen phosphate dodecahydrate, sodium molybdate dihydrate and sodium meta vanadate (all from M/s Loba Chemie, Mumbai), conc. H_2SO_4 and diethyl ether were used as received for the preparation of molybdovanadophosphoric acid. Phenol (M/s. S.D.Fine-chem., Mumbai), aqueous 30% H_2O_2 (M/s. E.Merck India Ltd, Mumbai) and acetonitrile of high purity were used without further purification. The exact strength of hydrogen peroxide was determined by redox titration against standard $KMnO_4$. The catalysts were prepared by methods described in Chapter 2.

8.2.2 Procedure

Procedure for the determination of strength of hydrogen peroxide

The peroxide content in the commercially available hydrogen peroxide is determined by the procedure described in Chapter 5.

Procedure for catalytic run

The liquid phase oxidation reactions were carried out in a two necked 50 ml round bottom flask immersed in a thermostated oil bath maintained at 65°C. A typical reaction mixture included phenol (1.88 gm, 20 mmol), aqueous hydrogen peroxide (2.36 gm, 20 mmol), catalyst (0.025 gm, 0.0125 mmol) and 2.10 gm acetonitrile. A magnetic stirrer was provided to stir the reaction mixture. The reaction mixture was subjected to GC analysis for product estimation. The effect of reaction parameters like catalyst concentration, temperature, solvent were on phenol hydroxylation were studied. The effect of molybdovanadophosphate salts with ammonium and tetrabutyl ammonium groups as the counter cations was studied and compared to that with the molybdovanadophosphoric acid (with proton as the counter cation) for phenol hydroxylation.

Analysis of products: The liquid products of phenol hydroxylation were analyzed on Shimadzu GC-14B using a HP-5 fused column with 30m x 0.53mx 1.5 μm film thickness and F.I.D detector.

8.3 Results and discussion

8.3.1 Catalyst characterisation

The molybdovanadophosphoric acids of the kind $H_4[PMo_{11}VO_{40}]$. nH_2O, $H_5[PMo_{10}V_2O_{40}]$ .nH_2O and $H_6[PMo_9V_3O_{40}]$ .nH_2O were characterised by thermal analysis, FTIR, UV- Visible and atomic absorption spectroscopy as described in chapter 5. The redox activity of vanadium substituted phosphomolybdic acids was studied by determining the redox potentials of these materials by cyclic voltammetry and comparing them with phosphomolybdic acid.

Characterisation of $[NH_4]_4[PMo_{11}VO_{40}]$ and $[(C_4H_9)_4 N]_4 [PMo_{11}VO_{40}]$

Thermal analysis

The water content in these complexes was determined by thermogravimetric analysis (given in fig.1) performed under the same conditions as the remaining catalysts.

$[NH_4]_4[PMo_{11}VO_{40}]$

The loss in weight due to water molecules is observed till 120.9°C which is about 5.42%. This indicates the total number of water molecules to be ≈ 6. Thereafter the loss in weight is attributed to the ammonium cation upto 459.1°C. Thereafter the compound was found to be stable.

$[(C_4H_9)_4\ N]_4\ [PMo_{11}VO_{40}]$

The thermogram for this compound displays very low loss mass due to water molecules. Only 0.31 % weight loss is attributable to water molecules which occurs at 204.2°C. This complex contains only 0.5 water molecules of water. The remaining drastic loss in weight is due to the tetrabutyl moiety upto approx. 450°C.

The phosphorus, molybdenum and vanadium content were determined by atomic absorption spectroscopy,

The microanalysis for the salts containing the ammonium and tetrabutyl ammonium groups as the counter cations was performed to determine the percentage of carbon, hydrogen and nitrogen.

Total elemental content was found as follows:

$NH_4[PMo_{11}VO_{40}]$: Nitrogen 2.76(2.86), Hydrogen 1.39(1.41), Phosphorus 1.38(1.58), Molybdenum 52.87(53.97), Vanadium 2.3(2.60), Oxygen 36.99(37.54)

$[(C_4H_9)_4N]_4[PMo_{11}VO_{40}]$: Carbon 27.78(27.88), Hydrogen 5.20(5.26), Nitrogen 2.01(2.03), Phosphorus 1.10(1.12), Molybdenum 38.30(38.31), Vanadium 1.79(1.84), Oxygen 23.42(23.52).

The values in brackets are the calculated %.

Infrared red spectroscopy

$NH_4[PMo_{11}VO_{40}]$

The infrared spectrum of this complex is almost similar to that of the molybdovanadophosphoric acid except that an extra peak is observed at 3220.9 cm^{-1} indicative of the N-H bond stretching.

$[(C_4H_9)_4N]_4[PMo_{11}VO_{40}]$

This compound shows bands peculiar to the Keggin anionic framework between the

1100 – 700 cm^{-1} range with a shoulder observed on the 1056.9 cm^{-1} band indicating the incorporation of vanadium into the framework as shown in fig.2 .

Cyclic voltammetry study

The cyclic voltammograms of phosphomolybdic acid and the mono vanadium substituted phosphomolybdic acid [both 1x 10^{-3}mol dm^{-3}] were taken in 50 % (v/v) water–acetonitrile medium containing 0.5 mol dm^{-3} H_2SO_4 as the supporting electrolyte. A glassy carbon electrode, a platinum wire and a saturated calomel electrode were used as working, counter and reference electrodes respectively. The voltammograms were recorded at ambient temperatures.

For phosphomolybdates it is difficult to obtain well – defined redox waves in cyclic voltammetry in aqueous electrolytes, due to the easy hydrolysis of $H_3PMo_{12}O_{40}$. Hence the complex is stabilised by addition of comparatively large amounts of organic solvents. Thus the voltammogram is usually measured in mixed organic-aqueous solvents containing acids.

In case of $H_3[PMo_{12}O_{40}]$ three redox couple were observed when the voltammograms were scanned from the potential range +0.6 to – 0.3 V at three scan rates i.e., 50, 100 and 200 mV/ seconds. The difference between the E_{pc} and E_{pa} is nearly equal to 60 mv which corresponds to a one electron reduction which is observed at all the three successive redox couple. The cathodic and anodic peak potentials (E_{pc} and E_{pa}) were found to be invariant with scan rate. Representative cyclic voltammetry data for 100 mv/ second run is given in table-1. The $E_{1/2}$ (half wave potentials) values were calculated as the average of the cathodic and anodic peak potentials for the oxidative and reductive waves. The ratios of cathodic and anodic peak currents were close to unity. The plots of cathodic peak currents v/s square root of scan rate passed through the origin suggesting that the process is diffusion controlled. The values are presented in table –1 and voltammograms in fig. 3.

Table – 1

Cyclic voltammetry data for $H_3PMo_{12}O_{40}$

Redox Couple	Cathodic Peak Potential E_{pc} (in V)	Anodic Peak Potential E_{pa} (in V)	Half Wave Potential $E_{1/2}$ (in V)
I	+0.28	+0.22	+0.25
II	+0.16	+0.11	+0.135
III	-0.08	-0.12	-0.10

Experimental conditions ; Working electrode: Glassy carbon, Counter electrode: Pt wire, Reference electrode: Saturated calomel electrode. Potential range: +0.6 to –0.3V. Current: 100μA. Scale: X axis = 100mv/cm Y axis = 250 mv/cm. +1VFS.

Cyclic voltammetry of molybdovanadophosphoric acid

Substitution of one molybdenum in the anionic framework by vanadium changes the nature of cyclic voltammogram. The cyclic voltammetry experiment of molybdovanadophosphoric acid was carried out under the same conditions as that for phosphomolybdic acid except that the potential sweep was conducted from +0.6 to –0.4 V for the former complex.

No clear voltammogram was obtained for the vanadium substituted complex at a lower scan rate of 50 mv/sec. But a well defined voltammogram was obtained at higher scan rates of 100 and 200 mv/sec. At these scan rates a flat wave like feature appears at +0.45 V with its analogues redox couple at +0.40 V. The introduction of vanadium into the complex has shifted the redox potential values to a more positive position. The standard electrode potential for the $V^{5+}/V4^{+}$ redox couple in acidic pH (3 –3.5) is +0.48V vs SCE. Techniques like ^{51}V NMR and ESR spectroscopy confirm the presence of both the oxidation states for the vanadium in the as synthesized samples. The Pourbaix diagram also indicates the presence of VO^{2+} and VO_2^+ at such low pH values (upto 4).

The rest of the peaks in this voltammogram are present as redox couple as given in table-2. The values of redox potentials for these peaks match for the molybdenum species in the complex.

Table – 1(a)
Cyclic voltammetry data for $H_4PMo_{11}VO_{40}$

Redox Couple	Cathodic Peak Potential E_{pc} (in V)	Anodic Peak Potential E_{pa} (in V)	Half Wave Potential $E_{1/2}$ (in V)
I	+0.45	+0.40	+0.425
II	+0.28	+0.11	+0.325
III	-0.08	-0.10	-0.09

Experimental conditions; Working electrode: Glassy carbon,
Counter electrode: Pt wire, Reference electrode: Saturated calomel electrode.
Potential range: +0.6 to –0.4V. Current: 100μA. Scale: X axis = 100mv/cm
Y axis = 250 mv/cm. +1VFS.

8.3.2 Catalytic activity

After the benzene hydroxylation studies, the catalytic activity of the mono, di and tri vanadium substituted phosphomolybdic acids was extended to substrates like phenol. The reaction when performed under the conditions mentioned in the experimental section gave a fairly good phenol conversion as given in table –2.

Table – 2
Catalytic activity of $H_{3+x}[PMo_{12-x}V_xO_{40}]$
for phenol hydroxylation

Catalyst	% Phenol conversion	% Product selectivity			TON
		Catechol	Hydroquinone	PBQ*	
PMo$_{11}$V	17.47	38.13	60.31	1.56	279
PMo$_{10}$V$_2$	16.34	34.48	63.63	1.89	261
PMo$_9$V$_3$	14.15	32.56	64.88	2.56	226

Conditions : Phenol (0.02 M), H_2O_2 (0.02M), Catalyst (0.0125mM), Acetonitrile (2.1 gm), Temperature (65^{o}C) and TON : Turn over number (mol substrate consumed per mol catalyst), Reaction time (1hr).

PBQ = *Para* benzoquinone

It is again seen that the mono vanadium substituted phosphomolybdic acid is the best performing of the above tabulated catalysts. The selectivity to para benzoquinone, the oxidation product of hydroquinone increases with the number of vanadium atoms in the catalyst.

The effect of reaction parameters like catalyst concentration, temperature, solvent were on phenol hydroxylation were studied. The effect of nature of counter cation was also studied. All the above mentioned factors were studied with PMo$_{11}$V as the catalyst.

No phenol hydroxylation occurred in the absence of a catalyst. There is no product formation in the absence of vanadium in the anionic framework of the phosphomolybdates. This suggests that vanadium is the active center for the catalytic reaction.

Effect of catalyst concentration

The catalyst concentration plays an important in the hydroxylation reaction. The substrate to catalyst molar ratio was 1600 for the reaction performed under conditions mentioned in table –2 which gave 17.47 % phenol conversion. The selectivity to the products i.e. catechol and hydroquinone was calculated to be 38.13 and 60.31 % respectively. The ratio was then reduced to 800. A net reduction in the value of phenol conversion was observed with increase in the concentration of the catalyst. A further reduction in the catalytic activity was observed when the ratio was reduced to 400 or the concentration of the catalyst was increased four times as in the initial reaction. The selectivity to para benzoquinone was found to increase with the catalyst concentration. The remaining reaction conditions were kept the same as given in table –2. So it was observed that the substrate conversion values reduced with the increase in the catalyst concentration which may be due to the fact that the rate of decomposition of hydrogen peroxide exceeds the process of oxidation. These results are tabulated below in table- 3.

Table – 3

Effect of catalyst concentration on phenol hydroxylation

Substrate: Catalyst (molar ratio)	% Phenol conversion	% Product selectivity			TON
		Catechol	Hydroquinone	PBQ	
1600	17.47	38.13	60.31	1.56	279
800	10.96	28.29	69.46	2.25	87
400	5.87	13.07	83.91	3.02	23

Effect of temperature

The temperature dependence on the hydroxylation of phenol was studied by performing the reaction at room temperature (35^{o}C), 65^{o}C and 80^{o}C. No products were formed at room temperature when the reaction was kept for two hours. As mentioned above about 17.5 % phenol conversion was obtained at 65^{o}C but the conversion level dropped to 14.16% when the reaction temperature was increased to 80^{o}C. It is interesting to note that the selectivity to the *para* product increased with temperature. The decrease in the reactivity with temperature may be attributed to the decomposition of hydrogen peroxide. The substrate phenol gave more selectivity to *para* benzoquinone at 80^{o}C. These results are given in table– 4.

Table – 4

Effect of temperature on phenol hydroxylation

Temperature (^{o}C)	% Phenol conversion	% Product selectivity			TON
		Catechol	Hydroquinone	PBQ	
35	–	–	–	–	–
65	17.47	38.13	60.31	1.56	279
80	14.16	19.33	76.77	3.90	226

Effect of counter cations

Compounds containing ammonium and tetrabutyl ammonium groups as the counter cation and a single vanadium atom substituted in the anionic framework were used as catalysts for phenol hydroxylation. Their catalytic activity was compared with complex containing proton as the counter cation. The former two compounds exhibited slightly lower activity compared to the acid (with proton as the cation). This suggests that Bronsted acidity is needed for phenol hydroxylation reaction, which decreases with salts containing ammonium and tetrabutyl ammonium groups as the counter cations. The results are given in table – 5

Table – 5

Effect of nature of counter cation on phenol hydroxylation

Counter Cation	% Phenol conversion	% Product selectivity			TON
		Catechol	Hydroquinone	PBQ	
H^+	17.47	38.13	60.31	1.56	279
NH_4^+	14.85	38.43	60.58	0.99	237
NBu_{4+}	14.72	40.11	59.0	0.89	235

8.4 Conclusions

We described in this chapter efficient phenol hydroxylation to catechol and hydroquinone and minor quantities of para benzoquinone with vanadium substituted phosphomolybdates in different reaction conditions, accomplished with hydrogen peroxide as the oxidant. The effect of different counter cations has been studied on phenol hydroxylation. The redox chemistry of vanadium substituted phosphomolybdates in the presence of hydrogen peroxide has been studied by cyclic voltammetry.

8.5 References

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SUMMARY

A novel class of heteropoly compounds, namely those of the Keggin structure, has attracted world wide attention as potential catalysts for organic reactions. The complexes with Keggin structure have the general formula $[XM_{12}O_{40}]^{n-}$ where X is the central / hetero atom M is the metal / addenda atom and n is the charge on the anion. The basic structure of Keggin type of heteropoly compounds consists of a tetrahedron with the hetero atom at its center surrounded by twelve octahedra in four sets. Each set contains three octahedral units. These octahedra are linked to each other and to the central tetrahedra through metal-oxygen bond linkages. The synthesis of this class of compounds can be tailored in a fashion suited for application in a particular reaction. Heteropoly compounds containing protons as the counter cation are known to be very strong acids having Bronsted type of acidity. Their acid strength is found to be greater than that of the mineral acids. Special properties associated with them like thermal stability, ease in synthesis and handling, high selectivity and good solubility facilitate their use in acid catalysed reactions.

The substitution of one or more metal atoms by another transition metal provides oxidation property to these compounds. The solubility of these transition metal substituted polyoxometalates, (T.M.S.P as they are called), can be controlled by selecting an appropriate counter cation. The most common counter cations include protons, alkali metals, alkyl ammonium groups, transition metals, etc. These compounds can be used under both homogeneous and heterogeneous reaction conditions with a wide variety of oxidants.

In the present work we have studied the oxidation properties of the Keggin

compounds

and utilized them as catalysts in liquid phase oxidation reactions. The study has been conveniently divided into eight chapters.

Chapter-1 : Introduction

After a brief information about the different types of heteropoly compounds, an account of the history of Keggin type heteropoly comlpexes is given. This is followed by the system of nomenclature, structural details and general properties of this class of polyoxometalates. The general methods of synthesis and characterization of these compounds are described in this chapter. The catalytic behaviour of Keggin heteropoly compounds with special emphasis being laid on the oxidation properties is discussed thereafter. An outline of the proposed work is also mentioned.

Chapter-2 : Experimental

In this chapter we discuss the synthesis of transition metal substituted heteropoly compounds. Preparation of the potassium salt of mono titanium substituted phosphotungstates is described which is followed by the disubstituted titanium complexes with tetrabutyl ammonium and dimethyl phenylbenzyl ammonium groups as the counter cations. The synthesis method for the potassium salt of dititanium substituted phosphotungstate supported on silica (10% w/w) is also described.

We have incorporated other transition metals like cobalt, copper and manganese in the silicotungstate lacunary framework and have also converted them to potassium salts. The chapter describes preparatory methods for the vanadium substituted phosphomolybdates having protons, ammonium and tetra alkyl ammonium groups as the counter cation.

The chapter also includes details of various characterization techniques used while working on the heteropoly compounds. The analytical techniques employed include micro analysis and atomic absorption spectroscopy. Physical techniques include

infrared, ultraviolet- visible and nuclear magnetic resonance spectroscopy to confirm the formation of the Keggin structure in the synthesized catalyst. Electron spin resonance spectroscopy was used as a tool to establish the oxidation state of the incorporated transition metal and the relative changes that occur during the reaction. The water content in the compounds was estimated by carrying out thermogravimetric analysis. The electrochemical properties of the vanadium substituted compounds were studied by cyclic voltammetry.

Chapter-3 : Olefin oxidation

This chapter describes oxidation of olefins such as cyclohexene and styrene. We have explained the role of isobutyraldehyde as reductant in the presence of titanium substituted phosphotungstates for the selective oxidation to epoxide along with the formation of some minor products in small quantities. Thus cyclohexene is oxidized to cyclohexene oxide in good yields along with traces of allylic oxidation products. Styrene is selectively oxidized to styrene oxide with the formation of oxidative cleavage product, i.e., benzaldehyde. The radical mechanism of the reaction is confirmed by the addition of a radical scavenger.

Chapter-4 : Oxidation of *p*-xylene

The oxidation of *p*-xylene is an industrially important chemical reaction. The production of terephthalic acid from *p*-xylene is achieved in industry using an homogeneous cobalt - manganese based catalyst with bromine compounds as promotors in acetic acid medium. In this chapter we discuss the utility of cobalt, manganese and copper substituted silicotungstates as catalysts in *p*-xylene oxidation in aqueous medium with air as oxidant. The advantage of our system is that it has been performed under mild and non-corrosive conditions. The product obtained in the first stage of oxidation is *p*-toluic acid, which is an intermediate in the formation of terephthalic acid.

Chapter-5 : Benzene hydroxylation

In this chapter we shift the attention to the use of vanadium substituted phosphomolybdates as efficient oxidation catalysts under homogeneous reaction conditions with hydrogen peroxide as the source of oxygen. Here we discuss an efficient benzene hydroxylation process with high yields of phenol under the reaction conditions. The reaction kinetics was performed and the mechanism confirmed by UV-Vis and ESR spectroscopy.

Chapter-6 : Cyclohexane oxidation

In this chapter we continue the description of molybdovanadophosphates as catalysts for cyclohexane oxidation in acetonitrile medium with hydrogen peroxide as oxidant under homogeneous reaction conditions. Oxidation with higher selectivity towards cyclohexanol has been achieved and a comparison of the efficiency of mono-, di- and tri-vanadium substituted catalysts has been carried out. The reaction mechanism was confirmed by performing *in situ* ^{51}V and ^{13}C NMR spectroscopy.

Chapter-7 : Synthesis, spectral and single crystal characterisation of tris tetrabutyl ammonium phosphododecamolybdate

The synthesis of the title compound was carried out and the single crystal isolated for X-ray diffraction study. The crystal belongs to triclinic space group. The crystal has a Keggin structure with tetrahedral PO_4 group at the center and the MoO_6 octahedra forming a heteropoly anion which is surrounded by three tetrabutyl ammonium cations. Other characterisation techniques such as IR, UV – Vis spectroscopy and thermal analysis have been used to confirm the Keggin structure.

Chapter-8 : Phenol hydroxylation

We describe in this chapter phenol hydroxylation to catechol and hydroquinone with

small quantities of para benzoquinone using vanadium substituted phosphomolybdates in different reaction conditions, accomplished with hydrogen peroxide as the oxidant. The effect of different counter cations has been studied on phenol hydroxylation. The redox chemistry of vanadium substituted phosphomolybdates has been studied by cyclic voltammetry.

Conclusion

The thesis briefly mentions the major findings of the study followed by logical conclusions derived from it. This study mainly includes liquid phase oxidation of organic substrates. We have laid emphasis on the reaction mechanism which is aptly supported by spectroscopic evidence. Thus the successful utilization of these compounds as oxidation catalysts promises a bright and a promising future for this class of compounds.