



## Heteropoly Acids and Related Compounds as Catalysts for Fine Chemical Synthesis

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# Heteropoly Acids and Related Compounds as Catalysts for Fine Chemical Synthesis

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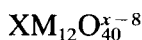
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*Key Words:* Acid and oxidation catalysis; Fine chemical synthesis; Heteropoly acids; Polyoxometalates.

## I. INTRODUCTION

Catalysis by heteropoly acids (HPAs) and related compounds is a field of growing importance, attracting increasing attention worldwide, in which many new and exciting developments are taking place in both research and technology [1–11]. HPAs are polyoxometalates incorporating anions (heteropolyanions) having metal–oxygen octahedra as the basic structural units [11–14]. Among a wide variety of HPAs those belonging to the so-called Keggin series are the most importance for catalysis. They include heteropolyanions (HPANs)



where  $\text{X}$  is the central atom ( $\text{Si}^{4+}$ ,  $\text{P}^{5+}$ , etc.),  $x$  is its oxidation state, and  $\text{M}$  is the metal ion ( $\text{Mo}^{6+}$ ,  $\text{W}^{6+}$ ,  $\text{V}^{5+}$ , etc.). These HPANs have a well-known Keggin structure which is composed of a central tetrahedron  $\text{XO}_4$  surrounded by 12 edge-sharing metal–oxygen octahedra  $\text{MO}_6$  (Fig. 1) [15]. The Keggin HPAs are the most stable and more easily available; these have been studied in more detail. Other heteropolymetalates—e.g., those with HPANs of the Dawson structure,  $\text{X}_2\text{M}_{18}\text{O}_{62}^{2x-16}$ ; Keggin and Dawson lacunary HPANs,  $\text{XM}_{11}\text{O}_{39}^{x-12}$  and  $\text{X}_2\text{M}_{17}\text{O}_{61}^{2x-20}$ ; and transition metal complexes thereof [11, 14]—are also used as catalysts. In this review HPAs are understood as the Keggin acids, unless otherwise stated. Generally, their formulas are abbreviated as  $\text{XM}$ , e.g.,  $\text{PW}$  and  $\text{SiW}$  for  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ , respectively. In addition to their well-defined structure [13, 14], HPAs have special properties which are of great value for catalysis, such as strong Brönsted acidity [4], ability to catalyze reversible redox reactions under mild conditions [1, 3], high solubility in water and oxygen-

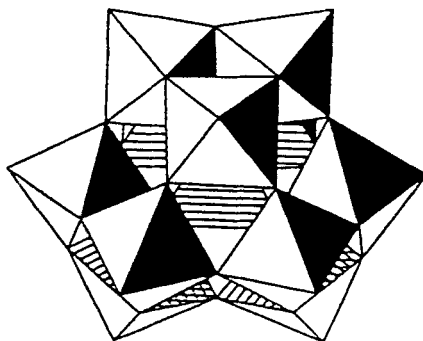


FIG. 1. The structure of the heteropolyanion  $\text{XM}_{12}\text{O}_{40}^{x-8}$  ( $\alpha$ -isomer) [15].

ated organic solvents, fairly high stability in the solid state, a "pseudoliquid phase" [7] (see later), etc. These properties render HPAs potentially promising acid, redox, and bifunctional catalysts in homogeneous as well as in heterogeneous systems.

In the last two decades, the broad utility of HPA acid and oxidation catalysis has been demonstrated in a wide variety of synthetically useful selective transformations of organic substances. The development of new effective catalytic systems as well as the understanding of mechanisms of HPA catalysis at the molecular level has been greatly advanced [2, 3, 7, 9, 11]. Remarkable progress has been made in the application of HPA catalysts. New industrial processes based on HPA catalysis such as oxidation of methacrolein, hydration of olefins (propene and butenes), and polymerization of tetrahydrofuran have recently been developed and commercialized [8].

A new promising field, less well documented so far, is the use of HPAs as catalysts for low-temperature organic reactions in the liquid phase, in particular for the synthesis of fine chemicals. A variety of quite efficient HPA-based syntheses of antioxidants, medicines, vitamins, etc., have been reported recently. The purpose of this review is to discuss the utility of HPAs as acid and oxidation catalysts for such organic reactions in homogeneous and heterogeneous liquid-phase systems. Such topics as HPA acid and redox properties, catalyst preparation and characterization, and mechanistic aspects of HPA catalysis are also surveyed. The review is addressed primarily to synthetic chemists in order to draw their attention to new opportunities created by the application of HPAs in synthetic practice. More detailed information about physicochemical and catalytic properties of HPAs can be found in monographs and reviews [1–14].

## II. ACID CATALYSIS

### A. Preparation of Heteropoly Acids

Preparation of HPAs is getting more and more important for their applications. Such HPAs as PW, SiW, and PMo are commercially available as crystalline hydrates. HPAs are usually prepared by acidifying an aqueous solution containing the salt of the heteroelement and the alkali metal molybdate or tungstate, with subsequent isolation of the HPA by extracting with ether or by ion exchange [12, 14]. As a rule, yields are not high, a large amount of waste products being formed.

Electrodialysis provides new opportunities for the synthesis of HPAs. An efficient electromembrane method has been developed for the preparation of PW, which is the most important acid catalyst in the HPA series [16, 17]. The HPA is formed in the anode compartment of dialyzer from  $\text{Na}_2\text{WO}_4$  and  $\text{H}_3\text{PO}_4$  in an aqueous solution (Fig. 2). The acidification

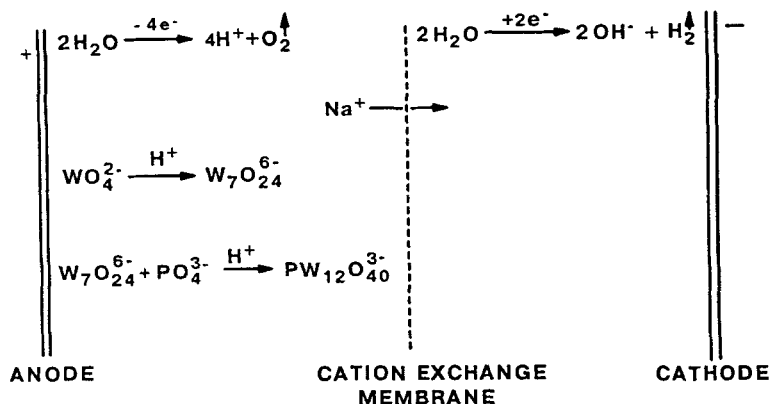


FIG. 2. The scheme of electromembrane synthesis of PW [16, 17].

needed is provided by electrolysis of water.  $\text{Na}^+$  ions are transferred by the electric potential from the anode to cathode through a cation-exchange membrane. As a result, pure PW at the anode and NaOH at the cathode are formed. The alkali obtained can be used to prepare Na tungstate from the starting  $\text{WO}_3$ . The HPA is isolated by crystallization in an almost 100% yield. No waste material is formed. Many other HPAs such as SiW,  $\text{PW}_{11}\text{Ti}$ ,  $\text{PW}_{11}\text{Zr}$ ,  $\text{PW}_{11}\text{Bi}$ ,  $\text{PW}_{11}\text{Ce}$ ,  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}$ , etc., can be prepared in a similar manner [17, 18].

## B. Characterization of HPA Catalysts

### 1. Proton Sites

HPAs are strong Brönsted acids [2–4]. Structural characterization of the HPA proton sites is an important step towards understanding the catalytic activity. The proton structure of HPAs has been discussed elsewhere [4, 7, 19]. Bond length–bond strength correlations [20] as well as  $^{17}\text{O}$  nuclear magnetic resonance (NMR) data [21] indicate that in the free polyanions in solution, the bridging oxygen atoms, having a higher electron density than the terminal oxygen atoms, are protonated. In the free Keggin anion, edge-bridging  $\text{M—O—M}$  oxygens are assumed to be the predominant protonation sites [Fig. 3(a)]. In solid HPAs, the protons take part in the formation of the HPA crystal structure, linking the neighboring HPANs. In this case the more accessible terminal oxygens can be protonated. Thus, from single-crystal x-ray and neutron diffraction data [22], the proton sites in the crystalline PW hexahydrate are represented as diaquahydrogen ions,  $\text{H}_5\text{O}_2^+$ , each of which links four neighboring HPAN's by forming hydrogen bonds with the terminal  $\text{W=O}$  oxygens [Fig. 3(b)]. In the dehydrated PW, according to  $^{17}\text{O}$  NRM data [23], the protons are also predominantly localized on the terminal oxygens. The structure of proton sites can be rep-

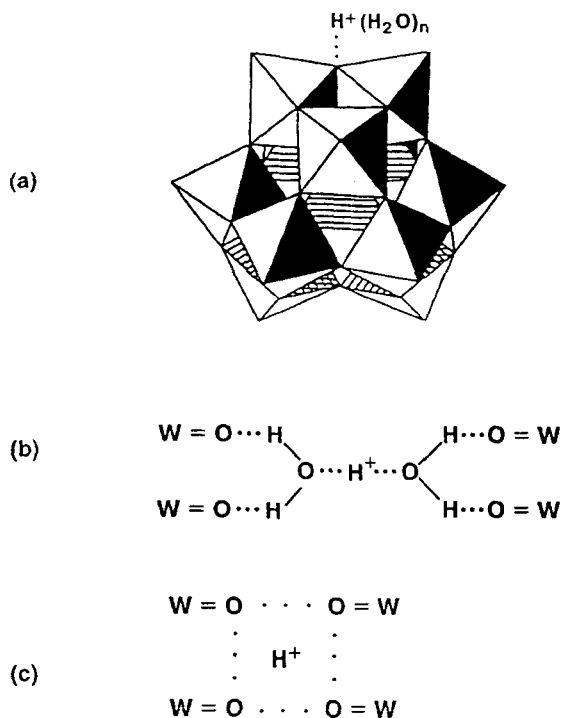


FIG. 3. Proton sizes in heteropoly acids: (a) HPA in solution [20]; (b) solid PW hexahydrate [22]; (c) solid dehydrated PW [23].

resented as shown in Fig. 3(c). This structure is assumed to be directly formed from the proton structure of the PW hydrate upon dehydration. Stoichiometrically, each proton is shared by four terminal oxygens like in PW hexahydrate, since all the terminal oxygens in the PW crystal lattice are apparently equivalent in  $^{17}\text{O}$  magic-angle spinning (MAS) NMR. It is suggested that the proton migrates between four equivalent positions,  $\text{W}=\text{O} \cdots \text{H}^+ \cdots \text{O}=\text{W}$ , and thus links four HPANs together, as does the  $\text{H}_5\text{O}_2^+$  ion in PW hexahydrate [Fig. 3(b)]. The same structure was suggested for the structurally similar HPA salts, e.g.,  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ , in which the  $\text{Cs}^+$  ions each have four equivalent terminal oxygens as the closest neighbors [22].

## 2. Acid Strength

In solutions, the acid properties of HPAs are well documented in terms of dissociation constants and Hammett acidity function [4]. The dissociation constants of HPAs were measured in such solvents as  $\text{H}_2\text{O}$  [24], and  $\text{Me}_2\text{CO}$ ,  $\text{EtOH}$ , and  $\text{AcOH}$  [25], etc.; the Hammett acidity function was determined in  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}-\text{AcOH}$ ,  $\text{H}_2\text{O}-\text{dioxane}$ ,  $\text{H}_2\text{O}-\text{EtOH}$  and  $\text{H}_2\text{O}-\text{Me}_2\text{CO}$  mixtures [26]. HPAs in solution are stronger than the usual mineral acids such as  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ , etc. (Table 1). The strength of the Keggin

TABLE 1  
Dissociation Constants of Heteropoly Acids in Acetone at 25°C [4]

Acid	pK <sub>1</sub>	pK <sub>2</sub>	pK <sub>3</sub>
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	1.6	3.0	4.0
H <sub>4</sub> PW <sub>11</sub> VO <sub>40</sub>	1.8	3.2	4.4
H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub>	2.0	3.6	5.3
H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	2.0	3.6	5.3
H <sub>4</sub> SiMo <sub>12</sub> O <sub>40</sub>	2.1	3.9	5.9
H <sub>2</sub> SO <sub>4</sub>	6.6	—	—
HCl	4.3	—	—
HNO <sub>3</sub>	9.4	—	—

HPAs depends weakly on their composition. Yet the tungsten acids are markedly stronger than molybdenum ones. The strongest and most stable acid in the Keggin series is PW [4]. The acidity of HPA concentrated solutions in terms of the Hammett acidity function also weakly depends on their composition and is higher than that of H<sub>2</sub>SO<sub>4</sub> [4].

Solid HPAs possess purely Brönsted acidity and are stronger than such conventional solid acids as SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>/SiO<sub>2</sub>, and HX and HY zeolites [27, 28]. The acid strength of crystalline HPAs decreases in the series:



which is identical with that in solutions (Table 1) [4, 7]. Usually, relative catalytic activities of HPAs are consistent with this order both in homogeneous and in heterogeneous systems [4, 7].

HPAs have moderately high thermal stability. The Keggin-type PW, SiW, PMo, and SiMo decompose at 465°, 445°, 375°, and 350°C, respectively [29]. The decomposition causes the loss of their activity. However, thermally decomposed molybdenum HPAs become reconstructed under exposure to water vapor [30, 31]. Under wet conditions, HPAs can hence be used as solid acid catalysts in vapor-phase reactions operated at relatively high temperatures.

According to microcalorimetric data [32], the proton sites in dehydrated PW are essentially uniform (Fig. 4). They are characterized by the differential heat of ammonia adsorption of 140–160 kJ/mol, which is almost the same as that for H-mordenite, one of the strongest acid zeolites. There is also a small amount (<3%) of stronger proton sites with the heat of ammonia adsorption above 170 kJ/mol. These are probably surface proton sites localized at the bridging O atoms in the Keggin unit. A recent microcalorimetric study [33] has examined the acid strengths of a number of HPAs by the sorption of NH<sub>3</sub> after pretreatment of the solids under various

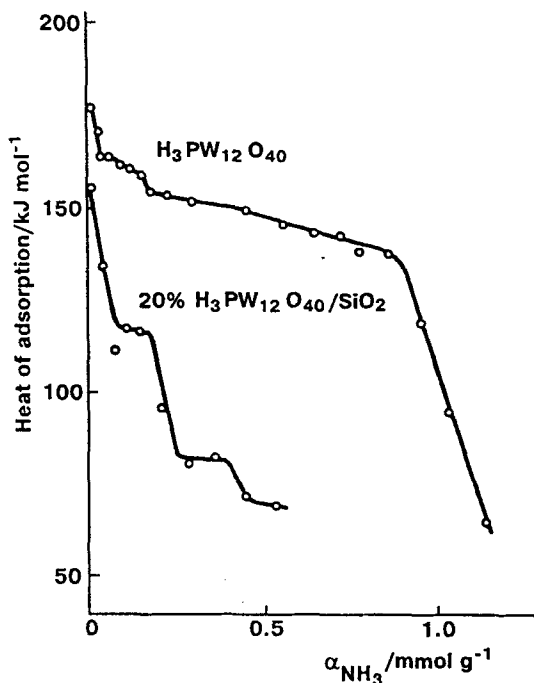


FIG. 4. Differential heats of  $\text{NH}_3$  adsorption at  $150^\circ\text{C}$  [32].

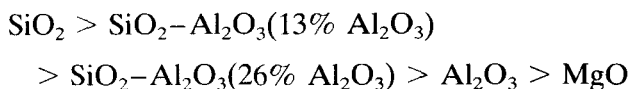
conditions. An effect of activation conditions was observed in that a lower activation temperature resulted in a higher differential heat of sorption but a lower number of acidic sites accessible for  $\text{NH}_3$ . This is explained by structural changes in solid HPAs and site blocking by water molecules (or  $\text{H}_5\text{O}_2^+$ ) as evidenced by thermogravimetry (TG), x-ray diffraction (XRD), temperature-programmed desorption (TPD), and  $^1\text{H}$  NMR. The order of acid strengths of solid HPAs, as determined by microcalorimetry at a sorption temperature of  $50^\circ\text{C}$  after pretreatment at  $150^\circ\text{C}$ , is  $\text{PW} \geq \text{SiW} \gg \text{PMo} \geq \text{SiMo}$ . Although there seems to be a parallelism of microcalorimetrically measured heats of  $\text{NH}_3$  sorption and maximum temperatures in the spectra of TPD of  $\text{NH}_3$  after activation at  $150^\circ\text{C}$ , it is suggested that of the two techniques, microcalorimetry is the more reliable method for elucidating the acid strength of HPAs [33].

### 3. Supported Heteropoly Acids

Supported HPA catalysts are important for applications because bulk HPAs have a low specific surface ( $1\text{--}5 \text{ m}^2\text{g}^{-1}$ ) [2, 4, 7, 9]. The catalytic activity of supported HPAs depends on the type of the carrier, the HPA loading, conditions of pretreatment, etc. Acidic or neutral substances such as  $\text{SiO}_2$  [34], active carbon [35, 36], acidic ion-exchange resin [37], etc., are suitable as supports, the most often used being  $\text{SiO}_2$ . Basic solids such as  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  tend to decompose HPA [7, 38]. For example, the catalytic



activity of supported PMo in the vapor-phase synthesis of methyl *t*-butyl ether from isobutene and methanol was found to decrease in the order of supports [38]:



In some cases the supporting inhibits the formation of coke. Thus bauxite-supported SiW was shown to coke less rapidly than the bulk HPA in the oligomerization of propene [39]. Also, diluting the bulk HPA catalyst with acid-washed sand (1 part catalyst to 10 parts sand) dramatically increased the liquid product yield and catalyst lifetime in the reaction at 250°C and 5 MPa pressure, but the acidity order remained the same as the pure bulk form [40].

SiO<sub>2</sub> is relatively inert towards HPAs, at least above a certain loading level, although some kind of chemical interaction takes place between HPA and SiO<sub>2</sub> (see below). The thermal stability of HPA on SiO<sub>2</sub> seems to be comparable to or slightly lower than that of the parent HPA [7, 41]. It was reported [42], however, that PMo became stable up to 600°C when supported on SiO<sub>2</sub>. On the other hand, thermally decomposed Keggin structure on the silica surface may be reconstructed on exposure to water vapor [31, 42].

As shown by microcalorimetry, when loading PW (20 wt%) on SiO<sub>2</sub>, the proton sites become weaker and less uniform (Fig. 4). Only 20% of the total number of proton sites remain as strong as in bulk PW. The rest have a differential heat of ammonia adsorption of about 120 kJ/mol, approaching that for acid sites of HX and HY zeolites [32]. According to ammonia thermal desorption data [32], the acid strength of supported PW decreases in the series of carriers: SiO<sub>2</sub> > α-Al<sub>2</sub>O<sub>3</sub> > activated carbon (Sibunit) (Fig. 5). At low loadings, PW and SiW form finely dispersed species on the SiO<sub>2</sub> surface; HPA crystal phase on silica is developed at HPA loading above 20 wt% [34, 43]. Various SiO<sub>2</sub> forms were observed on the silica surface by transmission electron spectroscopy (TEM): discrete molecules, clusters 50 Å in size, and large crystallites of 500 Å. Their relative amounts depend on the HPA loading [43].

SiO<sub>2</sub>-supported molybdenum HPAs, such as SiMo, PMo, and PMo<sub>10</sub>V<sub>2</sub>, retain the Keggin structure at high loadings but decompose at very low loadings due to their strong interactions with surface silanol groups [31, 41, 44–46]. A correlation was established between the catalytic behavior in the methanol oxidation/dehydration reaction and the state of SiMo and PMo on the silica surface [41, 44, 46]. At high loadings, the HPA has a behavior similar to that of the bulk HPA. In this case the acid catalysis predominates to yield dimethyl ether. On the other hand, at low loadings, when HPA decomposes to MoO<sub>3</sub>, losing the acidity, only redox catalysis is observed to give formaldehyde. For treatment temperatures under 240°C, these al-

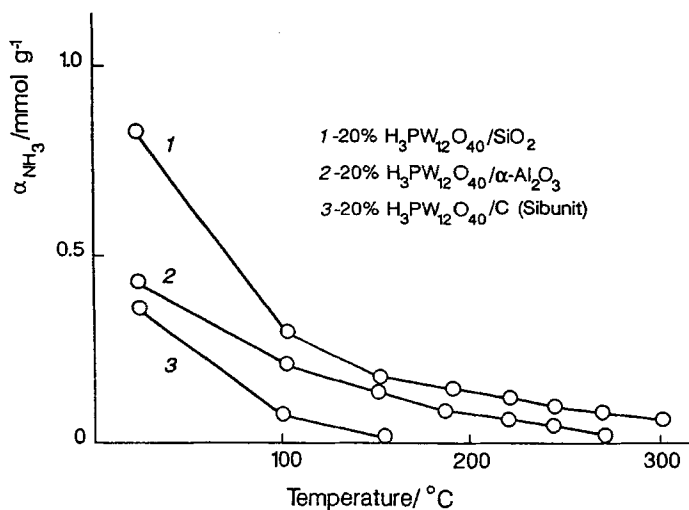


FIG. 5. Ammonia thermal desorption from supported PW catalysts [32].

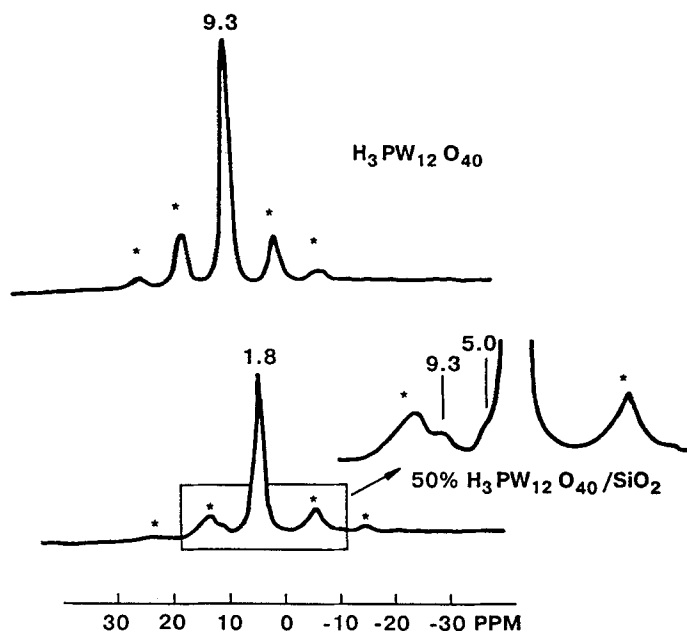


FIG. 6. <sup>1</sup>H MAS NMR spectra for bulk and SiO<sub>2</sub>-supported PW [48].

terations of the catalytic behavior occur between 0.1 and 0.2 monolayer coverage [44]. Similar behavior showed PMo<sub>10</sub>V<sub>2</sub> on SiO<sub>2</sub> [31].

Magic-angle spinning (MAS) NMR provides important information about solid HPA catalysts [47–51]. The proton MAS spectrum of bulk PW consists of one single isotropic line at 9.3 ppm (Fig. 6) [48]. In the spectrum

of the silica-supported PW, the most intense line at 1.8 ppm belongs to the silica OH groups. No line at 9.3 ppm typical for crystalline PW can be seen up to 50 wt% HPA content. However, at HPA content above 20 wt%, a new line at 5.0 ppm appears in the spectra. This indicates the interaction of HPA with silica and the formation of a new type of proton site on the silica surface [48]. The  $^{31}\text{P}$  MAS NMR spectra also indicate the interaction of PW with  $\text{SiO}_2$  [48, 50, 51]. The mechanism of this interaction is not yet clear. The silanol OH groups may participate in the HPA binding to form  $(\equiv\text{SiOH}_2^+)(\text{H}_2\text{PW}_{12}\text{O}_{40}^-)$  [51].

While weaker acids, HPAs supported on certain activated carbons are considered to be promising fixed-bed acid catalysts for liquid-phase reactions, e.g., esterification, because of their extraordinary stability towards HPA leakage from the carrier [35, 36]. As evidenced by IR and  $^{31}\text{P}$  MAS NMR, PW and SiW supported on a chemically ( $\text{H}_3\text{PO}_4$ ) activated carbon retain the Keggin structure at the HPA loading  $>5$  wt% but decompose at the lower loadings. HPAs form finely dispersed species on the carbon surface; no HPA crystal phase is developed even at an HPA loading as high as 45 wt% [52]. In contrast, on the silica surface, the HPA crystallinity appears already at 20 wt% HPA content. In  $^{31}\text{P}$  MAS NMR spectra of carbon-supported PW, a great line broadening was observed. This indicates a strong interaction of the HPA with carbon [52].

Solid acid catalysts having strong acid sites, regular structure, and a very narrow pore size distribution—e.g., zeolites and modified layered materials—have been most desirable because they are capable of strictly selecting reacting and product molecules by their size (size and shape selectivity). Recently, HPAs (PW) supported on a mesoporous pure-silica molecular sieve MCM-41 (BET surface area  $1200\text{ m}^2\text{g}^{-1}$ , uniform pores 32 Å in size) were prepared and characterized by nitrogen physisorption, x-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), and  $^{31}\text{P}$  MAS NMR [53]. The PW/MCM-41 compositions with PW loadings from 10 to 50 wt% have  $\sim 30$  Å uniformly sized mesopores. HPA retains the Keggin structure on the MCM-41 surface at an HPA loading above 20 wt%; at lower loadings a partial decomposition of PW was observed, probably due to interaction of PW with basic impurities in MCM-41. HPA forms finely dispersed species on the MCM-41 surface. No HPA crystal phase is seen at HPA loadings as high as 50 wt%. PW/MCM-41 exhibits a higher catalytic activity than  $\text{H}_2\text{SO}_4$  or bulk PW and shows a size selectivity compared to bulk PW and PW/ $\text{SiO}_2$  in liquid-phase phenol alkylation (see later).

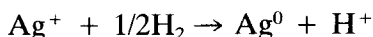
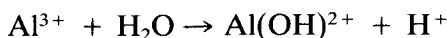
Pillared layered double hydroxides (“anionic clays”) were prepared by ion-exchange reaction of  $[\text{Zn}_2\text{Al}(\text{OH})_6]\text{NO}_3\cdot x\text{H}_2\text{O}$  with Keggin-type heteropolyanions [54]. Complete replacement of  $\text{NO}_3^-$  was achieved for Keggin anions, such as  $\text{PW}_9\text{V}_3\text{O}_{40}^{6-}$ ,  $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$ ,  $\text{SiW}_9\text{V}_3\text{O}_{40}^{7-}$ , etc., with a charge of  $-6$  or lower. No exchange was observed for anions such as  $\text{PW}_{12}\text{O}_{40}^{3-}$  and  $\text{SiW}_{12}\text{O}_{40}^{4-}$ . The intercalated anions below  $200^\circ\text{C}$  were accessible for catalytic

chemical conversions, e.g., for photocatalytic oxidation of isopropanol to acetone.

#### 4. Salts of HPAs

Water-insoluble HPA salts with certain monovalent cations, such as  $\text{NH}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ , etc., have high surface areas and microporous/mesoporous structures [55]. Even if these solids are prepared (by precipitation from aqueous solutions) to be stoichiometric, residual quantities of protons still remain, which are apparently responsible for the catalytic activity of these salts. Acidic Cs salt,  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}$ , due to its strong acid sites and high surface area ( $100\text{--}200\text{ m}^2\text{g}^{-1}$ ), is a remarkably efficient solid acid catalyst for a variety of organic reactions, especially promising for liquid-phase reactions [7, 56].  $\text{SiO}_2$ -bound  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}$  prepared through the hydrolysis of ethyl orthosilicate in the presence of colloidal  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}$  in ethanol is catalytically more active than Amberlyst-15 and H-ZSM-5, as based on the unit site [57]. Catalysts obtained by loading HPAs on their insoluble salts, e.g.,  $\text{PMo}/\text{K}_3\text{PMo}$ , have attracted interest recently [58, 59].

Certain "neutral" HPA salts can also gain proton sites upon interaction with the reaction medium. Two mechanisms of the proton generation in heteropoly salts are distinguished: the acidic dissociation of coordinated water (for salts with cations like  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ , etc.) and the reduction of the metal cation (for, e.g.,  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ , and  $\text{Pd}^{2+}$ ) [2, 7].



Ono [2] has reported that noble metal salts—e.g., Pt(II) and Pd(II) salts of PW—are capable of acting as bifunctional catalysts in alkane isomerization.  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}$  catalyzes the *n*-butane isomerization to isobutane [60]; combining the Cs salt with noble metals such as Pt enhances the activity in the presence of  $\text{H}_2$  [61].

### C. Mechanistic Features

#### 1. Homogeneous Catalysis

In principle, mechanisms of homogeneous catalysis by HPAs and by ordinary mineral acids are of the same origin. Both HPAs and mineral acids function as proton donors. There are, however, some specific features in the HPA catalysis. First, being stronger and, therefore, more efficient proton donors, HPAs are generally more active catalysts than mineral acids [4]. Second, HPAs play an important role in reaction promotion. On the one hand, HPAs can stabilize organic intermediates [9, 62]. On the other hand, they can cause a strong positive salt effect on the reaction rate [63].

To illustrate this, an excellent example is the hydration of isobutene,

an industrially important reaction. As a catalyst, concentrated aqueous solution of HPA is used. Compared to mineral acids, such as  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and  $\text{HClO}_4$ , HPA is more active per equal  $\text{H}^+$  concentration; HPA also shows a higher selectivity, minimizing side reactions such as isobutene oligomerization [62, 64].

Izumi et al. were the first to study the mechanism of this reaction [62]. They found that the reaction order with respect to HPA was dependent on the HPA concentration: first-order in diluted HPA solution and second-order in concentrated solution. In contrast, the reaction with mineral acids is first-order in the catalyst. A two-path reaction mechanism was suggested (Fig. 7). Path I is a commonly accepted mechanism with the formation of the intermediate carbenium ion. This mechanism does operate with mineral acids. Path II includes the formation of a complex of HPAN with olefin. It is path II that was assumed to be responsible for promoting the reaction and increasing the order with respect to HPA.

Alternatively, these data could be explained on the basis of the strong salt effect of HPANs. As found later [63], the rate of isobutene hydration catalyzed by HPAs obeys the Hammett plot (Fig. 8):

$$\lg k = -1.04H_0 - 3.46$$

And this plot is also valid for mineral acids such as  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{HClO}_4$ . This indicates that the reaction with both HPAs and mineral acids proceeds via the common mechanism (path I). The high order with respect to HPAs could be interpreted as being caused by the strong salt effect of HPANs. Whatever interpretation, the fact is that HPANs exhibit specific features which should be taken into account when considering homogeneous catalysis by HPAs.

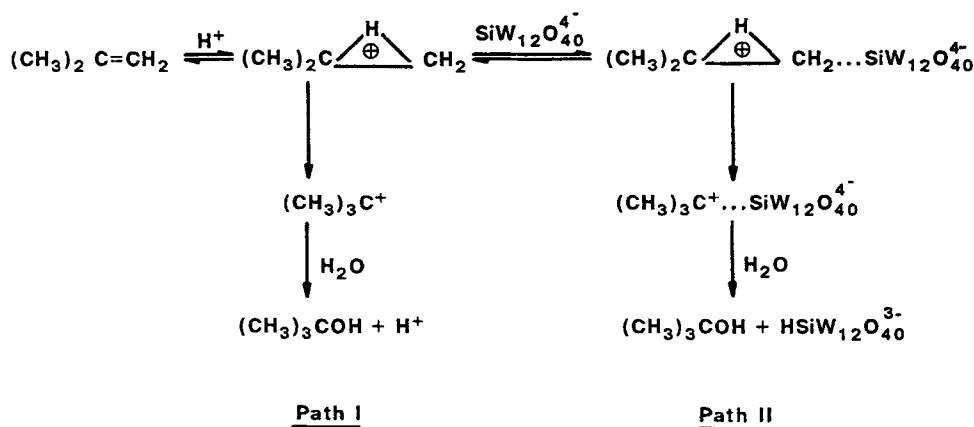


FIG. 7. The two-path mechanism for the hydration of isobutene catalyzed by HPA [62].

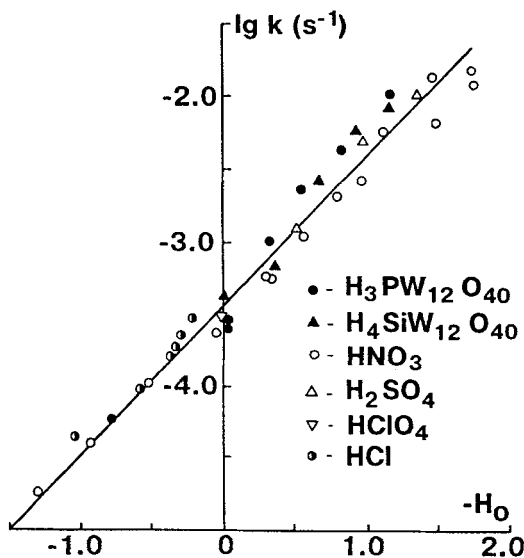


FIG. 8. The Hammett plot for the acid-catalyzed hydration of isobutene [63].

## 2. Heterogeneous Catalysis

In heterogeneous as well as in homogeneous systems, HPAs are generally more efficient catalysts than conventional ones such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2\text{-Al}_2\text{O}_3$ , HX and HY zeolites, etc. This is in full agreement with their relative acid strengths [2, 4, 7, 9]. Like other strong solid acids, HPAs are capable of generating carbenium ions from adsorbed olefins and arenes such as styrene, naphthalene, anthracene, etc. [65].

Misono et al. [7] demonstrated that crystalline HPAs in many respects behave like concentrated solutions. This is due to the fact that HPAs in solution as well as in the solid state have the same molecular structure (Keggin structure). Also of importance is the ability of solid HPAs to absorb a large amount of polar molecules—e.g., alcohols, ethers, amines, etc.—in the catalyst bulk as well as the extremely high proton mobility of solid HPAs. Generally, proton conductivities of solids correlate with the acid-base catalytic activities [66]. The mechanism of the proton conductivity of HPA hydrates has recently been discussed [66]. By virtue of the easy absorption of polar molecules, their catalytic reactions can occur not only on the surface, but also in the bulk of the crystalline HPA. Thus, towards polar substances, solid HPAs behave like highly concentrated solutions; i.e., all the HPA protons, not only the surface proton sites, participate in the catalytic reaction. This phenomenon, unusual for heterogeneous acid catalysis, is designated by the term “pseudoliquid phase” [7]. Unlike polar molecules, nonpolar reactants (e.g., hydrocarbons) are incapable of being

absorbed in the HPA bulk. They interact only with the surface of the catalyst. This pseudoliquid phase behavior apparently brings about high catalytic activities for a variety of reactions of polar molecules at low temperatures, i.e., when the sorption of the substrate in the catalyst bulk is high. Besides the activities, unique selectivities for dehydration of ethanol and conversion of dimethyl ether to hydrocarbons have been reported [7].

The uniformity of the pseudoliquid phase makes it feasible to use spectroscopic techniques to study the catalytic process. For instance, probable reaction intermediates of the ethanol dehydration such as protonated ethanol dimer  $(\text{EtOH})_2^+$ , monomeric  $\text{EtOH}_2^+$ , protonated ether, and ethoxide were directly identified in the pseudoliquid PW phase by solid-state NMR and IR spectroscopy [67].

#### D. Heteropoly Acids and Fine Chemical Synthesis

Since the majority of fine chemicals are complex, multifunctional molecules having high boiling points and limited thermal stability, their reactions are generally carried out in the liquid phase at moderate temperatures. In this context, HPAs have the following advantages over conventional acid catalysts [5]:

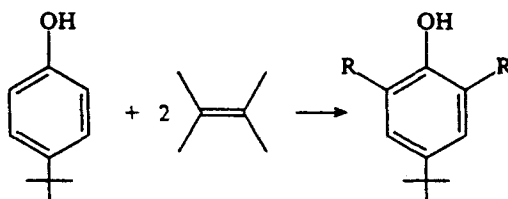
1. Being stronger acids, HPAs have a significantly higher catalytic activity in homogeneous and heterogeneous systems compared to  $\text{H}_2\text{SO}_4$ ,  $\text{SiO}_2\text{-Al}_2\text{O}_3$ , ion-exchange resins, etc.
2. Efficient operation under milder conditions.
3. In homogeneous systems, less alkali is needed to work up the reaction mixture and less waste is formed thereupon.
4. Lack of side reactions such as sulfonation, chlorination, nitration, etc., which take place with mineral acids in the liquid phase.

Either homogeneous or heterogeneous HPA catalysts can be used. HPAs therefore combine the high activity and selectivity usually associated with homogeneous catalysts with the ease of recovery and recycling that is characteristic of solid catalysts. Usually, tungsten HPAs are the preferred acid catalysts in the HPA series. This is due to their stronger acidity, higher hydrolytic and thermal stability, and lower oxidation potentials compared to the Mo and V acids [4]. In some cases, however (e.g., in the industrial hydration of olefins), Mo-HPAs can be used [8]. Prior to use, solid HPA catalysts are usually activated by heating *in vacuo* at  $200^\circ\text{--}250^\circ\text{C}$  for 1–2 h in order to remove water from HPA [4].

##### 1. Alkylation, Dealkylation, and Transalkylation of Phenols

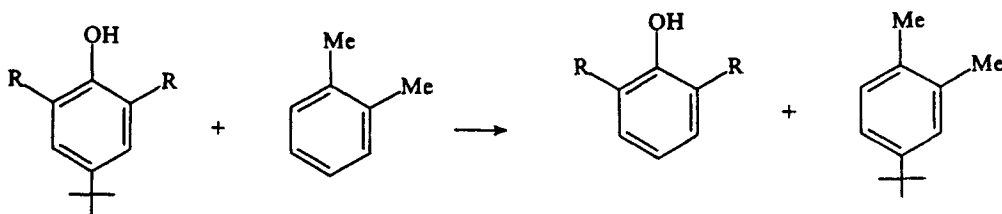
Alkylation, dealkylation, and transalkylation of phenols are widely used for manufacturing antioxidants, bioactive substances, etc. We have found that HPAs are the most versatile catalysts for these reactions.

HPAs catalyze the alkylation of benzene and alkylbenzenes with olefin [34, 68, 69]. Phenol is also readily alkylated with HPAs but not selectively [70–72]. 4-*t*-Butylphenol does react selectively with many olefins such as 1-hexene, cyclohexene, styrene, etc., as well as with benzyl chloride at 100°–150°C to give 2,6-dialkyl-4-*t*-butyl phenols in a 63–90% yield [70, 71]. Bulk



and SiO<sub>2</sub>-supported W-HPA's (1 wt% based on phenol) are the catalysts of choice in a heterogeneous liquid-phase system. They can be easily recovered and reused. The most selective is the alkylation with styrene, yielding 90% of the 2,6-dialkylated product at a 100% 4-*t*-butylphenol conversion (100°–110°C, 1 h). With  $\alpha$ -methylstyrene, the monoalkylation dominates, yielding 70% of 2-cumyl-4-*t*-butylphenol.

In the presence of *o*-xylene, which is the acceptor of *t*-butyl group, 2,6-dialkylphenols can be obtained in one step. For example, 2,6-dicyclohexylphenol is obtained in a 77% yield [70, 71]. *t*-Butylxylene formed in this reaction as a side product can be used in the synthesis of pigments.



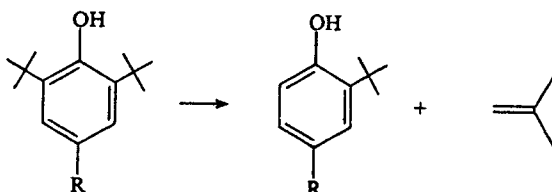
The alkylation of 4-*t*-butylphenol with olefins is suggested to proceed via a mechanism including the formation of ethers as primary products, followed by their subsequent rearrangement to the *C*-alkylated products. This mechanism is supported by detection of the ethers in the initial period of the reaction [70, 71].

PW supported (20–50 wt%) on a mesoporous siliceous molecular sieve MCM-41, having 30 Å uniformly sized pores, exhibits a higher catalytic activity than H<sub>2</sub>SO<sub>4</sub> or bulk PW and shows a size selectivity in alkylation of 4-*t*-butylphenol with olefins. In the alkylation with styrene, PW/MCM-41 gives higher yields of 2-(1-phenylethyl)-4-*t*-butylphenol than bulk PW or PW supported on amorphous silica, at the expense of the more bulky 2,6-*bis*-(1-phenylethyl)-4-*t*-butylphenol. HPA/MCM-41 is promising solid acid catalyst for conversion and formation of organic compounds of large molecular size [53].



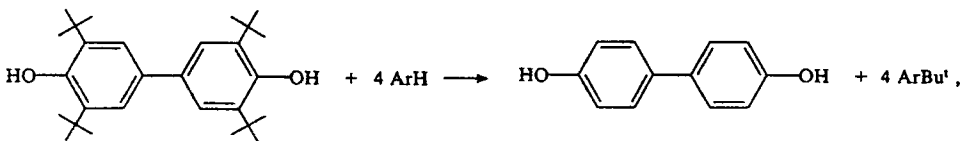
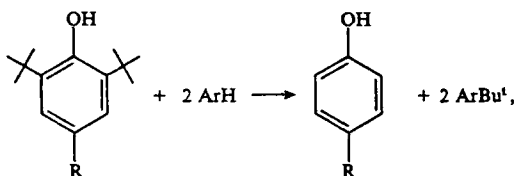
C-Alkylation of hydroquinone with isobutene to yield *t*-butylhydroquinone and 2,5-di-*t*-butylhydroquinone is catalyzed by  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ , and  $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}$  under phase-transfer conditions in a biphasic system, including toluene (upper phase) and HPA dioxane etherate,  $\text{HPA} \cdot x\text{C}_4\text{H}_8\text{O}_2 \cdot y\text{H}_2\text{O}$ , (lower phase) [73]. The yield of *t*-butylhydroquinone increases in the series:  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} < \text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71} < \text{H}_3\text{PW}_{12}\text{O}_{40}$ , with  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  being 70% (85°C).  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  has a higher efficiency than  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$ .

*t*-Butylation and de-*t*-butylation of phenols are widely used in synthetic organic chemistry as a method of positional protection. W-HPAs (<1 wt%) are efficient homogeneous and heterogeneous catalysts of the partial de-*t*-butylation of 2,6-di-*t*-butylphenols; see accompanying formula, where R =



H, Et, and  $\text{CH}_2\text{CH}_2\text{COOMe}$  [74, 75]. Mo-HPAs are deactivated in the course of the reaction due to their reduction by the reaction medium. In heterogeneous processes (100°–130°C), HPAs are 10s of times more active than such catalysts as ion-exchange resins, aluminosilicates, etc. In homogeneous processes (80°C), HPAs are >100 times more active than  $\text{H}_2\text{SO}_4$ . The catalytic activity of HPAs correlates with their acid strengths.

Bulk and silica-supported W-HPAs (0.5–7 wt%) are versatile catalysts for the complete trans-de-*t*-butylation of phenols at 100°–140°C [76, 77]; see accompanying formulas, where R = H, Me, Et,  $\text{CH}_2\text{CH}_2\text{COMe}$ ,



$\text{CH}_2\text{CH}_2\text{COOMe}$ ,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{OCOMe}$ ,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ , and  $\text{CH}_2\text{CH}_2\text{CH}_2\text{OCOC}_{17}\text{H}_{35}$ . The reaction occurs with a 92–98% yield. Toluene and *o*-xylene are the best acceptors of *t*-butyl group. The catalyst can

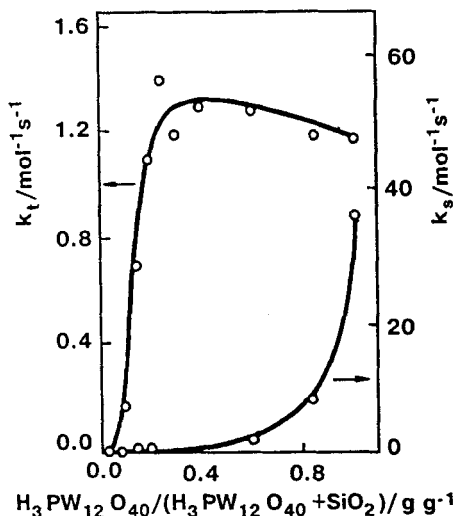
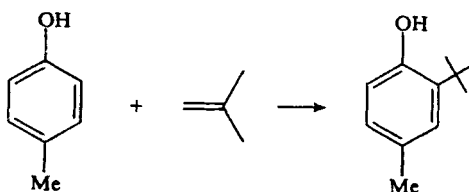


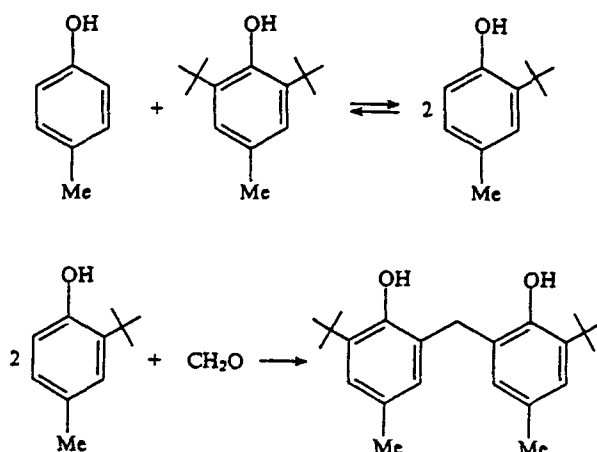
FIG. 9. Dependence of the rate constants  $k_t$  and  $k_s$  on the PW loading [77].

be easily recovered without neutralization and reused. Again, HPAs show much higher activity compared to conventional catalysts. Even Nafion-H, a polymeric perfluororesinsulfonic acid comparable in its strength to 100%  $\text{H}_2\text{SO}_4$  [78], is less active than PW in this reaction.

The trans-de-*t*-butylation of phenols is first-order with respect to both phenol and HPA [77]. With  $\text{SiO}_2$ -supported catalysts, the rate depends dramatically on HPA loading (Fig. 9). The rate constant  $k_t$ , based on the total amount of HPA protons in the catalyst, increases with increasing HPA loading, passing a maximum at 30 wt% HPA loading. Assuming the surface-type catalysis mechanism, this dependence is explained as a result of the competitive influence of enhancing the acid strength and reducing the number of the surface proton sites as the HPA loading increases. Analogous dependence was observed for the vapor-phase dehydration of *t*-butanol over PW and PMo [79]. By contrast, the rate constant  $k_s$ , based on the amount of the HPA surface protons, increases monotonously with HPA loading as the acid strength increases. Thus there is a fair correlation between the catalytic activity and catalyst acid strength.

A commercial alkylation of *p*-cresol with isobutene with the use of PW instead of  $\text{H}_2\text{SO}_4$  has been developed in Russia [5]. It is the first step in the synthesis of an antioxidant 2,2'-methylene-bis-(6-*t*-butyl-4-methylphenol), which is widely used for stabilizing polymers. Two versions of the



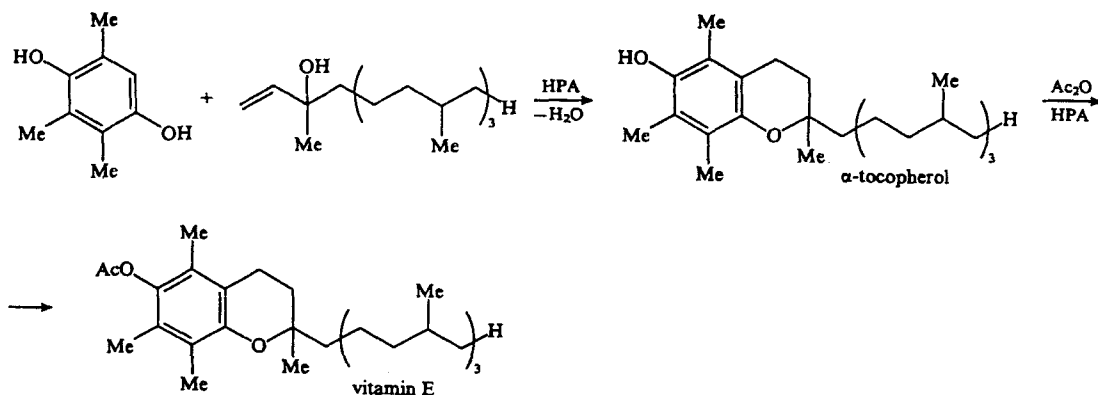


*p*-cresol alkylation are used; straight alkylation with isobutene and transalkylation with 2,6-di-*t*-butyl-4-methylphenol. The final step—the condensation of 2-*t*-butyl-4-methylphenol with formaldehyde—is carried out in a usual way with HCl as a catalyst. The use of HPA provides the gain in selectivity of 7–10% and almost completely eliminates water pollution in the first step of the process. Industrial application started in 1986.

## 2. Condensation

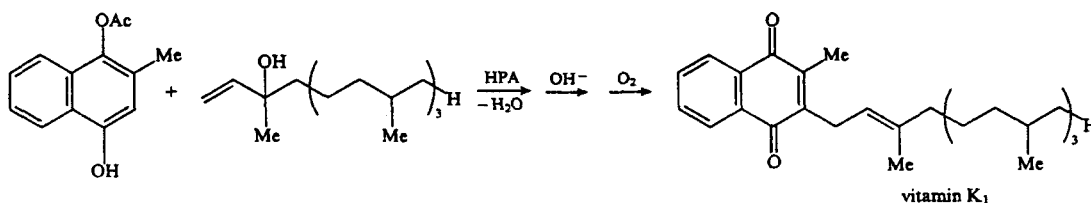
HPAs have long been known as catalysts for condensation reactions, e.g., the condensation of acetone to mesityl oxide and alkylbenzenes [80, 81] and the condensation of ketones and phenols to bisphenols [82].

Recently, we have used HPAs as catalysts for condensations in the synthesis of vitamins E, K<sub>1</sub>, and C [83, 84]. PW and SiW catalyze the condensation of isophytol with 2,3,5-trimethylhydroquinone (TMHQ) to  $\alpha$ -tocopherol as well as the acetylation of  $\alpha$ -tocopherol to its acetate (vitamin E) [83]. Both homogeneous and heterogeneous systems operate, with ca.



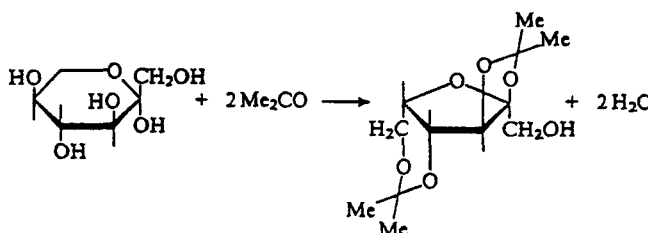
1 wt% HPA based on TMHQ being charged. Commercial synthesis of  $\alpha$ -tocopherol is carried out with the use of  $\text{H}_2\text{SO}_4$  or  $\text{ZnCl}_2$  as catalysts. With  $\text{ZnCl}_2$  (20 wt% on TMHQ), which is the best catalyst, a high-quality product containing 95% vitamin E is obtained in a 80% yield. The drawback to this process is the high consumption of the catalyst and a large amount of waste products. With HPAs (1 wt%), the yield of vitamin E is 10% higher and the quality of the product obtained is not lower than that obtained with  $\text{ZnCl}_2$ . HPAs can be recovered from the reaction mixture and reused. This method has been successfully tested on a pilot scale.

HPAs are also active in a similar reaction of isophytol condensation,



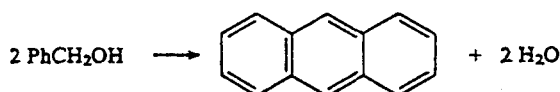
which is a key step in the synthesis of vitamin K<sub>1</sub> [83]. HPAs are 50 times as active as  $\text{ZnCl}_2$  and  $\text{Al}_2\text{O}_3\text{-SiO}_2$ .

Acetonation of L-sorbose is a step in the synthesis of L-ascorbic acid (vitamin C). The acetonation protects the internal OH groups of sorbose from oxidation. This reaction proceeds smoothly in acetone solution in the presence of 0.1 wt% PW or SiW as a homogeneous catalyst, yielding 85% diacetone-L-sorbose [84]. (See formula.) Water formed is absorbed by a



zeolite or distilled off. In industry, oleum is used in a large excess as both the catalyst and desiccant. The yield is about 80%. The disadvantage of this method is a large quantity of waste  $\text{Na}_2\text{SO}_4$  obtained after the oleum neutralization.

Bulk PW and SiW catalyze the condensation of benzyl alcohol to anthracene but less efficiently than such solids as HY zeolite and fluorinated alumina [85]. The reason for the lower activity of HPAs may be their small

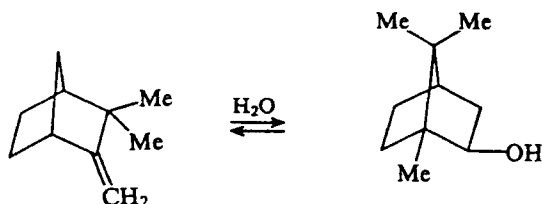


specific surface and lack of Lewis acid sites if such sites are required for the reaction.

### 3. Hydration and Dehydration

HPA catalyzed hydration of  $C_2$ – $C_4$  olefins can be carried out in the liquid and or vapor phase [4]. As mentioned earlier, the hydration of propene and butenes is now used in industry to produce alcohols [8].

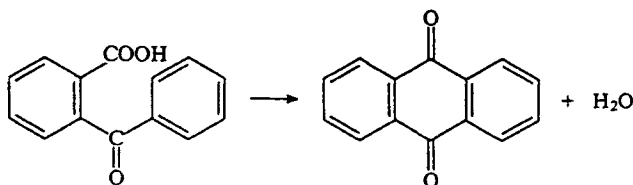
PW and SiW are efficient catalysts for the homogeneous hydration of camphene to isoborneol, which is an intermediate in the synthesis of camphor [86]. The reaction proceeds at  $50^\circ\text{C}$  in  $\text{Me}_2\text{CO}$ – $\text{H}_2\text{O}$  solution. Iso-



borneol is formed almost exclusively at camphene conversion up to 35%. With  $\text{H}_2\text{SO}_4$ , under comparable conditions, the reaction rate is far lower and the conversion of camphene does not exceed 3%. The stronger acid, PW has a slightly higher activity than SiW. The direct one-step hydration of camphene to isoborneol may be of practical interest because the current procedure is a two-step process via an intermediate product, bornyl acetate.

Cycloalkenes are hydrated to cycloalkanols with a  $>99\%$  selectivity in the presence of a catalyst consisting of a concentrated aqueous solution of an arylsulfonic acid and W-HPA [87]. HPAs were reported to be more efficient catalysts than  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  in the hydration of phenylacetylene [88].

PW can be used instead of  $\text{H}_2\text{SO}_4$  as a catalyst of the dehydration of



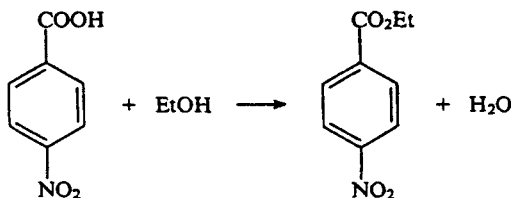
*o*-benzoylbenzoic acid to anthraquinone [89].

### 4. Esterification and Etherification

Homogeneous liquid-phase esterifications, transesterifications, and ester decompositions have been extensively studied in the presence of Keggin and Dawson HPAs as catalysts [4, 9, 90, 91]. Generally, the catalytic ac-

tivities follow the order of the acid strength of the solutions of HPAs. Water greatly affects the rate of these reactions [91]. Molybdenum HPAs can be deactivated due to their reduction by the reaction medium [90].

Esterification of *p*-nitrobenzoic acid is a step of the anesthetic synthesis. Ethyl-*p*-nitrobenzoate is obtained in a 99% yield by esterification of *p*-nitrobenzoic acid with ethanol in the presence of PW (3–7 wt%) at 75°C [5]. Water formed in the reaction course is separated by azeotrope with



toluene. Initially homogeneous, the reaction mixture becomes a two-phase system in the end of the reaction: The upper phase contains the product; the lower phase is a concentrated solution of HPA in ethanol. Thus, the catalyst is easily separated and can be reused.

Esterification of dipicolinic acid (DA) with butanol, which is a step of the synthesis of pharmaceuticals, is catalyzed by PW as well as by its insoluble salts [92]. PW (1 wt%) as a homogeneous catalyst is almost as efficient as



sulfuric acid, yielding 100% of the DA diester (118°C, 3 h). The acidic Ce(III) salt, Ce<sub>0.87</sub>H<sub>0.4</sub>PW, practically insoluble in butanol, has been found to be fairly active as a heterogeneous catalyst to give a 100% yield of the DA diester (5.4 wt%, 118°C, 4 h). Although less active than the parent HPA, Ce<sub>0.87</sub>H<sub>0.4</sub>PW can be easily separated and reused. Insoluble NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup> salts of PW showed moderate activities in this reaction. The activity decreases in the series: Ce<sub>0.87</sub>H<sub>0.4</sub>PW >> Cs<sub>2.5</sub>H<sub>0.5</sub>PW > Cs<sub>3</sub>PW > Cs<sub>2</sub>HPW > (NH<sub>4</sub>)<sub>3</sub>PW > K<sub>3</sub>PW. The mechanism of Ce<sub>0.87</sub>H<sub>0.4</sub>PW catalysis remains unknown; both Brønsted and Lewis acid sites may be important.

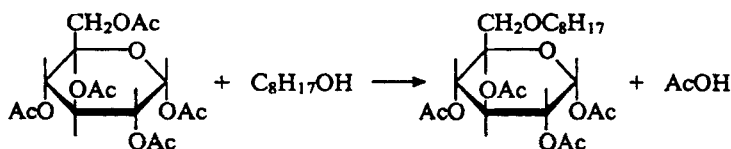
Cs<sub>2.5</sub>H<sub>0.5</sub>PW was reported to be more active for liquid-phase ester decomposition than such solid-acid catalysts as Nafion-H, HY, and H-ZSM-5 zeolites, and SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> [93].

HPAs, both bulk and supported on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, or TiO<sub>2</sub>, catalyze the formation of hydroquinone (HQ) monoethers [94], which are used in the synthesis of medicines, perfumes, stabilizers, etc. For example, the reaction of HQ with 1-hexanol in the presence of PMo (3%) gives the monoether with a 99% selectivity at 83% HQ conversion (105°C, 5 h).

Dialkyl phthalates, widely utilized as plasticizers, were obtained by

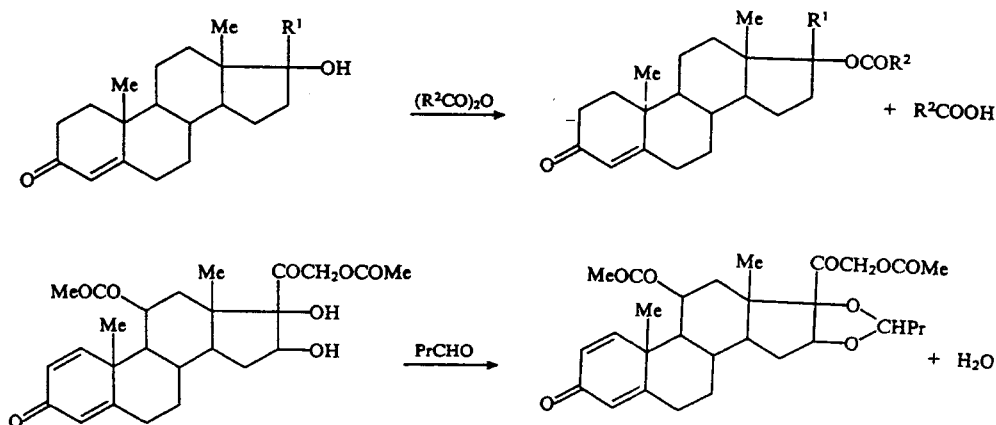
esterification of phthalic anhydride with  $C_8$ – $C_{10}$  alcohols at  $100^\circ$ – $120^\circ\text{C}$  in the presence of PW (1–2%) as a homogeneous or heterogeneous catalyst [36]. In the latter case, activated carbon was used as a carrier. The catalytic activity of the HPA is significantly higher than that of  $\text{H}_2\text{SO}_4$  and *p*-toluenesulfonic acid. HPA/C is less active than the homogeneous PW catalyst, but it can be easily separated from the reaction mixture and reused.

Synthesis of glycosides catalyzed by HPAs is of industrial importance [8]. Many patents cover this reaction. Thus monosaccharides interact readily with alcohols in the presence of HPAs ( $85^\circ\text{C}$ , 4 h), yielding 47–83% of glycosides [95]. For example, octyl tetraacetylglycoside is obtained from glucose pentaacetate and 1-octanol with PMo (3%) in a 70% yield. Gly-



cosides are used as new effective and biodegradable surfactants.

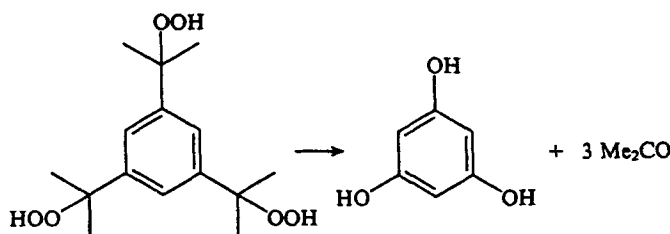
Esterification and acetalization of steroids (e.g., testosterone,  $17\alpha$ -hydroxyprogesterone, etc.) are catalyzed by bulk and  $\text{SiO}_2$ -supported HPAs (1.5–9%) [96]. These reactions occur with a quantitative yield at  $40^\circ$ – $82^\circ\text{C}$ . HPAs show almost the same activity as  $\text{HClO}_4$ . These reactions are interesting for the preparation of modified hormones.



### 5. Miscellaneous Reactions

PW and SiW catalyze the acylation of aromatic compounds (Friedel–Crafts reaction) [97, 98].  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}$  shows high efficiency as an insoluble solid-acid catalyst in acylation, e.g., in  $(\text{PhCO})_2\text{O}$  + *p*-xylene; this catalyst is about 20 times as active as PW [99].

HPAs have long been known as very efficient catalysts for the decomposition of cumene hydroperoxide to phenol and acetone [100, 101]. Similarly, 1,3,5-trihydroxybenzene is formed via the decomposition of 1,3,5-tri-isopropylbenzene hydroperoxide at 50°–100°C with a 97% selectivity and a 89% hydroperoxide conversion [102].



The hydrolysis of sucrose is catalyzed by SiW [103].

### III. POLYOXOMETALATES IN LIQUID-PHASE OXIDATION

The liquid-phase oxidation of organic substances catalyzed by polyoxometalates proceeds in homogeneous or two-phase aqueous–organic systems, O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, alkylperoxides, etc., being applied as oxidants. In contrast to acid catalysis, where easily available classical Keggin-type HPAs dominate, in liquid-phase oxidation, a wide variety of polyoxometalates are used, such as isopolyanions and heteropolyanions. A promising direction is the use of metal-substituted polyoxometalates as robust metalloporphyrin analogs in oxidation chemistry [11]. Catalysis by polyoxometalates in liquid-phase oxidation has been reviewed elsewhere [1, 2, 3, 9–11, 104, 105].

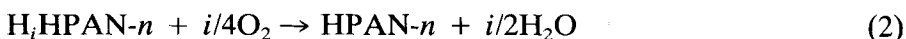
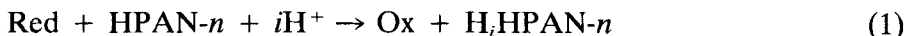
#### A. Oxidation with Dioxygen

Matveev et al. first demonstrated that in these reactions mixed molybdovanadophosphoric heteropolyanions, PMo<sub>12-n</sub>V<sub>n</sub>O<sub>40</sub><sup>(3+n)-</sup> (HPAN-*n*, *n* = 2–6), are the most versatile catalysts [1, 3, 104]. They have a fairly high oxidation potential (0.7 V relative to normal hydrogen electrode) and are capable of oxidizing a number of organic and inorganic substances. At the same time, HPAN-*n* are reversibly acting oxidants; i.e., their reduced forms can be readily reoxidized to the parent HPAN-*n* by O<sub>2</sub> under rather mild conditions. Hence a wide variety of liquid-phase oxidations have been carried out with using HPAN-*n* as the catalyst and O<sub>2</sub> as the oxidant. Some other heteropolyanions having similar properties, e.g., PMo<sub>6</sub>W<sub>6</sub>O<sub>40</sub><sup>3-</sup>, can also be used for this purpose [106, 107].

Generally, such catalytic reactions proceed via a stepwise Mars–van Krevelen-type mechanism, i.e., stoichiometric oxidation of the substrate



followed by reoxidation of the reduced form of the oxidant with dioxygen:



Here Red and Ox are, respectively, the  $i$ -electron reductant (substrate or the reduced form of a cocatalyst) and its oxidized form (product or the oxidized form of the cocatalyst), and  $\text{H}_i\text{HPAN-}n = [\text{H}_i\text{PMo}_{12-n}\text{V}_{n-i}^{\text{S}+}\text{V}_i^{\text{4}+}\text{O}_{40}]^{(3+n)-}$  is the reduced form of HPAN- $n$  ( $i < n$ ). It is the V atom in HPAN- $n$ , alternating between  $\text{V}^{\text{S}+}$  and  $\text{V}^{\text{4}+}$  during the redox transformations, which is responsible for the redox properties of HPAN- $n$ . Reactions (1) and (2) can be carried out in the same reactor or separately. When separately, direct contact between the substrate and  $\text{O}_2$  is excluded [1, 3, 104]. This constitutes a useful (particularly for fine chemicals synthesis) alternative, which combines the advantages of stoichiometric oxidants (high selectivities and broad scope) with those of catalytic oxidation with  $\text{O}_2$ .

As the catalysts, either one-component systems (i.e., HPAN- $n$  themselves) or two-component systems are used. The most important two-component system includes HPAN- $n$  and Pd(II) [1, 3]. This system is analogous to the well-known Wacker catalyst based on  $\text{CuCl}_2$  and Pd(II) for oxidation of olefins to carbonyl compounds, e.g., for the oxidation of ethylene to acetaldehyde. In contrast to the  $\text{CuCl}_2 + \text{Pd(II)/Pd(0)}$  catalytic system, the HPAN- $n + \text{Pd(II)/Pd(0)}$  system can work at a very low concentration of  $\text{Cl}^-$  or even in the absence thereof. Hence HPAN- $n + \text{Pd(II)}$  has the advantage of being more active, more selective, and less corrosive. Usually the HPAN- $n + \text{Pd(II)}$  system operates via the mechanism involving Eqs. (1) and (2) [1, 3, 104].

Other two-component catalytic systems based on HPAN- $n$ —e.g., those including Ti(III)/Ti(I) [108], Pt(IV)/Pt(II) [109], Ru(IV)/Ru(III), Ir(IV)/Ir(III) [110],  $\text{Br}_2/\text{Br}^-$  [111], and  $\text{I}_2/\text{I}^-$  [112] redox couples—are also known. HPAN + Pd(II) and HPAN + Rh(I) were used in carbonylation, hydroformylation and hydrogenation reactions [113–117].

HPAN- $n$  aqueous solutions are extremely complex systems. These systems contain a number of species such as heteropolyanions and isopolyanions as well as monomeric products of their decomposition, existing in equilibrium with the parent HPAN- $n$  [3]. Recently Pettersson [118] has characterized the equilibria in the five-component system  $\text{H}^+ - \text{Mo(VI)} - \text{V(V)} - \text{V(IV)} - \text{P(V)}$  (especially in  $\text{PMo}_{10}\text{V}_2$  and  $\text{PMo}_9\text{V}_3$  solutions) by a combined EMF–NMR method. In principle, various species which are present in such systems may be catalytically active. Thus, in oxidation of  $\text{H}_2\text{S}$  with  $\text{PMo}_{12}\text{O}_{40}^{3-}$  at pH 3, isopolyanions  $\text{Mo}_7\text{O}_{24}^{6-}$  or  $\text{Mo}_8\text{O}_{26}^{4-}$  were assumed to play an active role [119]. In the oxidation of olefins, alkylbenzenes, and phenols by  $\text{O}_2$  in the presence of HPAN- $n$ , the active species is likely

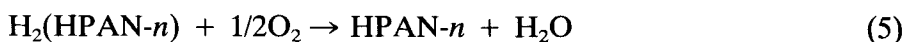
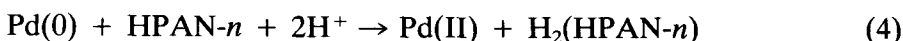
to be the  $\text{VO}_2^+$  ion formed as a result of the dissociation of HPAN-*n* [1, 120, 121].

The  $\text{VO}_2^+$  ion is hardly oxidized by  $\text{O}_2$  in acidic aqueous solutions but it is readily oxidized when incorporated in the HPAN-*n* coordination sphere [Eq. (2)]. This reaction is suggested to proceed via a multielectron transfer in the complex of  $\text{H}_i\text{HPAN-}n$  with  $\text{O}_2$  followed by the protonation of the heteropolyanion [3].

### 1. Oxidation of Olefins

One of the most important aerobic liquid-phase oxidations catalyzed by HPAN-*n* includes Wacker reactions, i.e., oxidation of olefins to carbonyl compounds [1]. The Wacker process is usually carried out using the  $\text{Pd(II)} + \text{CuCl}_2$  catalyst system in aqueous solution at  $100^\circ\text{--}130^\circ\text{C}$ . This process has several drawbacks such as formation of environmentally objectionable chlorinated by-products and strong corrosion of the reactor. The chlorinated by-products mainly arise from chlorinations by  $\text{CuCl}_2$ , their yields being 2%, 7%, and 25% for the oxidation of ethylene, propylene, and butylene, respectively. Thus the replacement of  $\text{CuCl}_2$  by a chloride-free oxidant has long been desired.

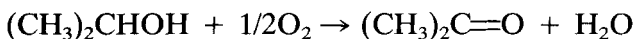
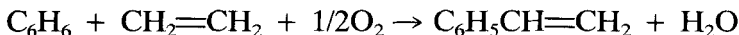
Matveev et al. [1, 3] first proposed the use of HPAN-*n* with  $\text{PdSO}_4$  as a chloride-free catalyst system in the Wacker oxidation of olefins to carbonyls—ethylene to acetaldehyde and higher olefins to ketones. The reaction proceeds in an acidic aqueous solution at a pH 0.5–2.0. The oxidation of ethylene can be represented by Eqs. (3)–(5):



Izumi et al. [106] found that the Wacker oxidation of 1-butene was effectively catalyzed by another chloride-free system,  $\text{PdSO}_4 + \text{H}_3\text{P-Mo}_6\text{W}_6\text{O}_{40}$ .

Catalytica has developed new technology for the Wacker oxidation of ethylene and higher olefins with the use of the  $\text{Pd(II)} + \text{HPAN-}n$  system [122]. In order to enhance the reaction rate and to stabilize palladium in solution, the reaction is carried out in the presence of  $\text{Cl}^-$  ions at a very low concentration (5–25 mM). This technology has been applied to acetaldehyde manufacture in a two-stage Wacker-type plant, having separate ethylene and air reactors. In this process, over 99% of the production of chlorinated by-products is eliminated, decreasing to less than 0.01% yield on ethylene.

Other examples of liquid-phase oxidations catalyzed by the  $\text{Pd(II)} + \text{HPAN-}n$  system include acetoxylation and arylation of olefins, oxidation of alcohols, etc. [3].

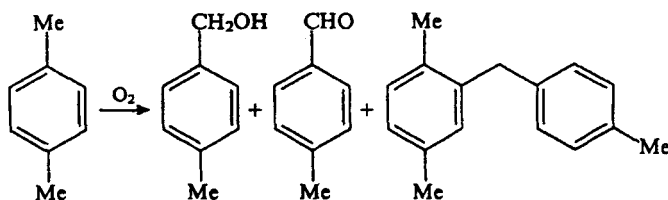


Neumann [123] reported that  $\text{PMo}_{10}\text{V}_2\text{O}_{40}^{5-}$  (as one-component catalyst) catalyzed the aerobic oxidative dehydrogenation of dienes to aromatics as well as of alcohols to ketones, amines to Schiff bases, and phenols to diphenoquinones. The dehydrogenation of  $\alpha$ -terpinene to *p*-cymene was found to be zero-order in  $\alpha$ -terpinene, first-order in dioxygen, and second-order in  $\text{PMo}_{10}\text{V}_2\text{O}_{40}^{5-}$  [124]. On the basis of these kinetic results and spectroscopic data, a reaction scheme was formulated. The scheme involves the formation of a stable substrate-catalyst complex in the catalyst reduction (substrate oxidation) stage and a  $\mu$ -peroxo catalyst intermediate in the catalyst reoxidation stage where dioxygen is reduced in a four-electron redox reaction.

Ishii et al. [125] and Mizuno et al. [126] have reported that heteropolyoxometalates catalyze the epoxidation of olefins by dioxygen in the presence of aldehyde. Thus various olefinic compounds are selectively epoxidized with dioxygen (1 atm, 25°C, 4 h) in the presence of 2 equiv of 2-methylpropanal and a catalyst for which the idealized formula is assumed to be  $(\text{NH}_4)_5\text{H}_4\text{PMo}_6\text{V}_6\text{O}_{40}\cdot 6\text{H}_2\text{O}$  [125]. This method has also been applied to the epoxidation of allylic and homoallylic alcohols as well as to the Baeyer-Villiger oxidation of cyclic ketones. In the absence of olefins, the aldehydes are converted into the corresponding carboxylic acids. The selective epoxidation of olefins by  $\text{O}_2$  is also catalyzed at 25°C by transition metal substituted 12-tungstophosphates,  $\text{PW}_{11}\text{O}_{39}\text{M}^{x-}$ , where  $\text{M} = \text{Co}, \text{Mn}, \text{Fe}, \text{Cu}$  or  $\text{Ni}$ , whose activity decreases in that order [126]. The order of the effectiveness of the aldehydes is: pivalaldehyde > isobutyraldehyde >> butyraldehyde  $\approx$  acetaldehyde > valeraldehyde > benzaldehyde. The catalytic activity of  $\text{PW}_{11}\text{Co}$  is solvent dependent, decreasing in the series:  $\text{CHCl}_3 > \text{CH}_2\text{Cl}_2 > 1,2\text{-C}_2\text{H}_4\text{Cl}_2 \approx \text{CH}_3\text{CN} > \text{C}_6\text{H}_6 > \text{DMF} > \text{DMSO}$ .

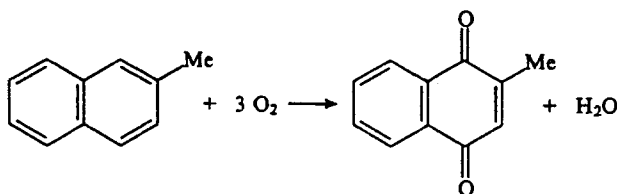
## 2. Oxidation of Arenes

Heteropolyanions oxidize methylbenzenes in acetic acid solutions to give a mixture of benzylic alcohols, aldehydes, and di- and polyaryl methanes. Under  $\text{O}_2$ , the reaction proceeds catalytically. The active oxidizing species are probably the  $\text{VO}_2^+$  ions formed via the dissociation of HPAN-*n*. The oxidation rate decreases in the series arenes: durene > mesitylene



> *p*-xylene > toluene. The reaction apparently proceeds via the formation of aromatic radical cations as intermediates [120].

2-Methylnaphthalene (MN) is oxidized to 2-methyl-1,4-naphthoquinone by O<sub>2</sub> (3–8 atm) in the presence of 0.02–0.2 M HPAN-*n* as the catalyst in an AcOH–H<sub>2</sub>O–H<sub>2</sub>SO<sub>4</sub> solution at 120°–140°C with a 82% selectivity and 78% MN conversion [127]. 2-Methyl-1,4-naphthoquinone is an intermediate in the synthesis of K vitamins. Traditionally it is manufactured by the stoichiometric oxidation of MN with CrO<sub>3</sub> in a low yield (40–50%).

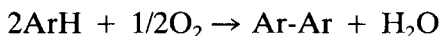


Heteropolyanions catalyze the oxidative bromination of arene nuclei—e.g., benzene and derivatives thereof, naphthalene, thiophene, etc.—with HBr as the brominating agent and O<sub>2</sub> as the oxidant.



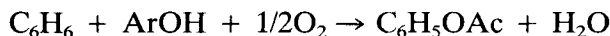
The reaction proceeds in an AcOH–H<sub>2</sub>O–H<sub>2</sub>SO<sub>4</sub> solution at 50°–100°C. The probable active brominating species is Br<sub>2</sub>, which is formed as a result of the Br<sup>−</sup> oxidation by HPAN-*n*. The advantage of this method is the possibility of using Br<sup>−</sup> in the reaction instead of Br<sub>2</sub> [111]. The HPAN-*n* + HBr system selectively brominates phenol in the para position [128].

The oxidative coupling of arenes in the presence of the HPAN-*n* + Pd(II) system as the catalyst provides a convenient one-step method of obtaining biaryls, which are valuable intermediates in organic synthesis:



where ArH = PhH, PhAlk, PhCl, PhCOOH, PhCF<sub>3</sub>, thiophene, etc. [129–131]. The reaction proceeds under mild conditions at 50°–90°C and an O<sub>2</sub> pressure of 1.5 atm with a 70–93% selectivity to biaryls. In the absence of HPAN-*n*, the Pd(II)-catalyzed arene coupling requires a temperature of 150°C and an O<sub>2</sub> pressure of 25 atm [104]. The mechanism of the oxidative coupling of arenes has been discussed elsewhere [132].

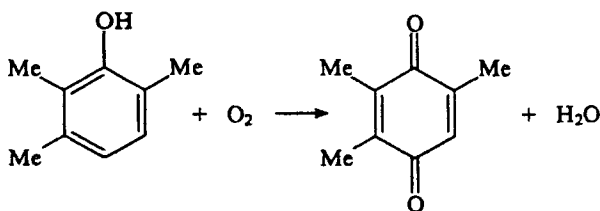
The acetoxylation of ArH is catalyzed by Pd(OAc)<sub>2</sub> + H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> with the additives of NaOAc [3].



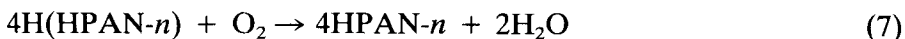
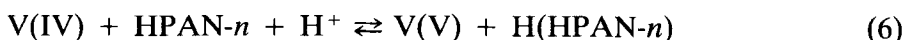
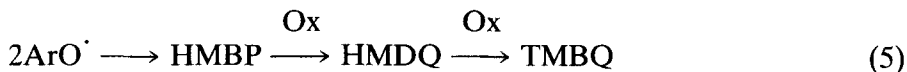
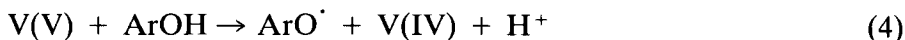
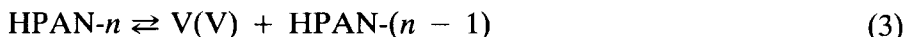
### 3. Oxidation of Phenols

The oxidation of 2,3,6-trimethylphenol (TMP) to 2,3,5-trimethyl-1,4-benzoquinone (TMBQ) is of practical interest as a step of the synthesis of vitamin E. The oxidation of TMP by O<sub>2</sub> with HPAN-*n* as the catalyst in

aqueous acetic acid solution gives TMBQ in a 86% selectivity at 100% TMP conversion [121]. The coupling product, 2,2',3,3',6,6'-hexamethyl-4,4'-bi-

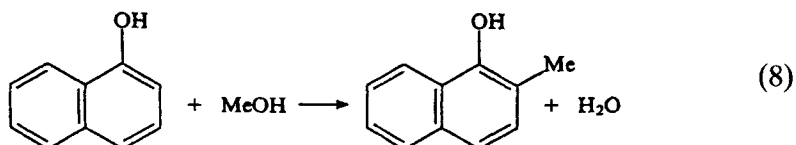


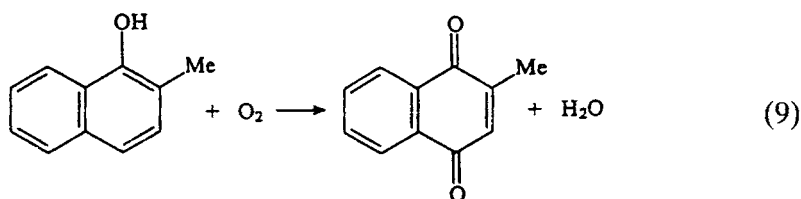
phenol (HMBP), is also formed. The yield of TMP depends on the water content in the reaction mixture; with [H<sub>2</sub>O] increasing, the yield of HMBP increases at the expense of TMBQ. HMBP, in turn, is oxidized to TMBQ, probably via the intermediate formation of hexamethyldiphenoquinone (HMDQ). There has been evidence that the catalytically active species is the VO<sub>2</sub><sup>+</sup> ion formed as a result of the HPAN-*n* dissociation. The mechanism of TMP oxidation can be represented by Eqs. (3)–(7). One-electron oxidation of TMP (ArOH) by VO<sub>2</sub><sup>+</sup> to form phenoxyl radical is probably the rate-limiting step. Further transformations of the phenoxyl radical give TMBQ as the final product. V(IV) formed in the reaction is oxidized to V(V) by O<sub>2</sub> in the HPAN-*n* coordination sphere.



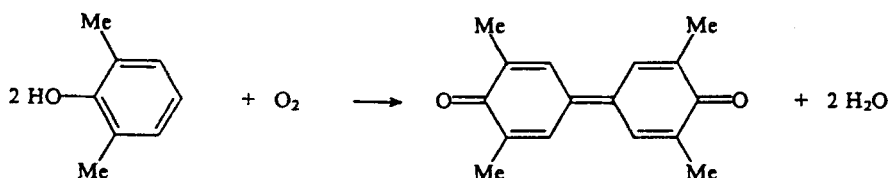
A new two-step method of the synthesis of vitamin K<sub>3</sub> from 1-naphthol has been developed [133]. It involves the vapor-phase alkylation of 1-naphthol by methanol to 2-methyl-1-naphthol followed by the liquid-phase oxidation of the latter to 2-methyl-1,4-naphthquinone by O<sub>2</sub> catalyzed by HPAN-*n*. The selectivities of reactions (8) and (9) are >90% and >83%, respectively. This method could be an attractive alternative to the conventional stoichiometric oxidation of 2-methylnaphthalene by CrO<sub>3</sub>.

Many metal complexes catalyze the oxidative coupling of phenols to diphenoquinones in solutions [134]. The coupling of 2,6-dialkylphenols cat-





alyzed by copper amine complexes is of practical importance for the synthesis of stabilizers. In this reaction, HPAN-*n* shows a higher activity than



copper complexes. The oxidative coupling proceeds in  $\text{H}_2\text{O}$ ,  $\text{AcOH-H}_2\text{O}$ , or  $\text{MeOH-H}_2\text{O}$  as solvents at  $25^\circ\text{--}50^\circ\text{C}$  under  $\text{O}_2$  pressure of 1–5 atm. Diphenoquinones, insoluble under these conditions, can be readily isolated from the reaction mixture by crystallization. Thus, 2,2',6,6'-tetramethyl- and 2,2',6,6'-tetra-*t*-butyl-diphenoquinones have been obtained in 100% yield. The catalyst can be recycled without loss of its activity [135].

### B. Oxidation with Hydrogen Peroxide

Tungsten and molybdenum polyoxometalates catalyze various oxidations of organic substances by hydrogen peroxide such as epoxidation of olefins, oxidation of alcohols, glycols, phenols, etc., in homogeneous or two-phase systems [2, 9, 10]. In the two-phase systems, phase-transfer catalysts are used to promote the oxidations. Peroxopolyoxometalates have been shown to be the active intermediates in these reactions [136–138].

The oxidation of allyl alcohol by  $\text{H}_2\text{O}_2$  in aqueous solution in the presence of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  gives glycerol in 64–100% yield based on  $\text{H}_2\text{O}_2$  charged ( $70^\circ\text{--}90^\circ\text{C}$ , pH 0.7–1.8, 1–2 h). The primary product is probably the epoxide, which is rapidly hydrolyzed to glycerol in acidic medium. Probable reaction intermediates, peroxy complexes of  $\text{PW}_{12}\text{O}_{40}^{3-}$ , containing up to four peroxy groups linked to the Keggin anion, were detected in the reaction medium by  $^{31}\text{P}$  NMR [136].

Tungsten heteropolyanions such as  $\text{PW}_{12}\text{O}_{40}^{3-}$ ; the lacunary anion  $\text{PW}_{11}\text{O}_{39}^{7-}$ ; and its complexes with transition metal ions of the formula  $\text{PW}_{11}\text{O}_{39}\text{M}^x-$ —where  $\text{M} = \text{Ni(II)}, \text{Co(II)}, \text{Cu(II)}, \text{Fe(II)}, \text{Cr(III)}, \text{Ru(IV)}, \text{Ti(IV)}$ , and  $\text{V(V)}$ —have been examined as the catalysts of homogeneous epoxidation of cyclohexene in acetonitrile at  $35^\circ\text{C}$ . The anion  $\text{PW}_{11}\text{O}_{39}^{7-}$  shows the highest catalytic activity and selectivity to the epoxide. The anion  $\text{PW}_{12}\text{O}_{40}^{3-}$  is much less active. The  $\text{Co(II)}$ ,  $\text{Cu(II)}$ , and  $\text{Ru(IV)}$  complexes

are inactive in the oxidation of cyclohexene but readily decompose  $\text{H}_2\text{O}_2$ . Neither epoxidation nor decomposition of  $\text{H}_2\text{O}_2$  takes place with the Ni(II), Ti(IV), and V(V) complexes. The Fe(II) and Cr(III) complexes are moderately active in the oxidation of cyclohexene but the reaction is not selective [137].

Cyclopentene is oxidized by hydrogen peroxide to glutaraldehyde in the presence of Keggin HPAs in tributylphosphate (TBP) solution at  $35^\circ\text{C}$ . The yield of glutaraldehyde based on  $\text{H}_2\text{O}_2$  (mol%) decreases in the HPA series:  $\text{H}_3\text{PMo}_{10}\text{W}_2\text{O}_{40}$  (61) >  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  (47) >  $\text{H}_4\text{GeMo}_{12}\text{O}_{40}$  (21) >  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$  (6) >  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (5) >  $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$  (1) [139].

Two-phase systems including immiscible aqueous and organic phases, such as 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$ , etc., are widely used in oxidations by  $\text{H}_2\text{O}_2$  catalyzed by polyoxometalates [139–145]. Tetraalkylammonium ( $\text{C}_6$ – $\text{C}_{18}$ ), cetylpyridinium, and other cations ( $\text{Q}^+$ ) with phase-transfer function are employed as phase-transfer catalysts. Active peroxopolyoxometalates are formed in the aqueous phase from the W(VI) or Mo(VI) starting compounds (e.g., heteropolyanions or  $\text{WO}_4^{2-} + \text{PO}_4^{3-}$ , etc.) and hydrogen peroxide. The initial heteropolyanions can then partly decompose on the interaction with the excess  $\text{H}_2\text{O}_2$ . With the phase-transfer catalyst,  $\text{Q}^+$ , the peroxopolyoxometalates are almost fully transferred into the organic phase because their  $\text{Q}^+$  salts are readily soluble in organic solvents. The reaction takes place preferentially in the organic phase via the oxygen atom transfer from the peroxopolyoxometalate to the substrate. The peroxopolyoxometalates are regenerated at the interface by the interaction with  $\text{H}_2\text{O}_2$ . The mechanism of the two-phase epoxidation of olefins by hydrogen peroxide in the presence of  $\text{PW}_{12}\text{O}_{40}^{3-}$  is illustrated schematically in Fig. 10.

Tetrahexylammonium heteropoly-11-tungstates are active catalysts for the oxidation of cyclohexene by 30% aqueous  $\text{H}_2\text{O}_2$  in the 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ – $\text{H}_2\text{O}$  system. The reaction proceeds in the organic phase. The main product

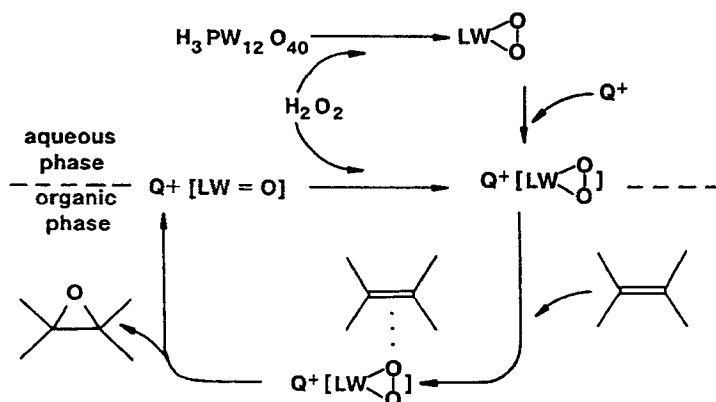
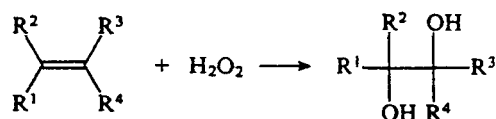


FIG. 10. Epoxidation of olefins by hydrogen peroxide in a two-phase system.

is cyclohexandiol, the oxidative cleavage products—adipaldehyde and adipic acid—also being formed. In contrast to the lacunary anions, the parent Keggin HPANs show much lower activity, if any [141].

Venturello et al. [138, 140] have reported that tetrakis(diperoxotungsto)phosphate,  $(Q^+)_3[PW_4O_{24}]^{3-}$ , where  $Q^+ = N(C_6H_{13})_4^+$ ,  $N(C_8H_{17})_3(CH_3)^+$ , etc., is remarkably effective in stoichiometric as well as in catalytic two-phase epoxidation of olefins with  $H_2O_2$ . This compound was isolated and characterized by x-ray diffraction [138]. The anion  $PW_4O_{24}^{3-}$  has the  $C_2$  symmetry and consists of the central  $PO_4$  tetrahedron linked through its oxygen atoms to two pairs of edge-sharing distorted pentagonal bipyramids  $W(O_2)_2O_3$  (Fig. 11). Each tungsten atom is linked to two peroxide groups located in the equatorial plane of the pentagonal bipyramid. It is noteworthy that  $W(VI)$  and  $Mo(VI)$  have the same coordination environment in their monomeric diperoxo complexes, which effectively epoxidize olefins [144].

The epoxidation of 1-octene with 15%  $H_2O_2$  in the presence of  $PW_4O_{24}^{3-}$  in the 1,2- $C_2H_4Cl_2-H_2O$  system affords epoxyoctane in 89% yield (based on the initial  $H_2O_2$ ) at a 100%  $H_2O_2$  conversion (70°C, 1.5 h). The reaction is stereoselective: *cis*-hex-2-ene is converted solely into the *cis*-epoxide, while *trans*-hex-2-ene gives the *trans*-epoxide [138].  $PW_4O_{24}^{3-}$  also catalyzes the two-phase oxidation of olefins to water-soluble vicinal *trans*-glycols in 71–88% yield (60°–70°C, 1–4 h, 2–4%  $H_2O_2$ , pH 1.2–1.5), as



shown in the accompanying formula, where  $R^1-R^4 = H, Me, Et, Bu, Ph$ , etc. [143]. The glycols formed are present almost entirely in the aqueous phase and can be readily isolated from the reaction mixture. The vicinal

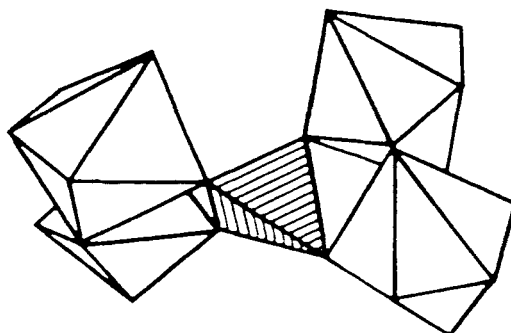


FIG. 11. The structure of peroxoheteropolyanion  $PW_4O_{24}^{3-}$  (from data in Ref. 138).



glycols are used for the preparation of cosmetics, perfumes, photographic materials, etc.

The epoxidation of 1-octene by hydrogen peroxide in the  $\text{CHCl}_3\text{-H}_2\text{O}$  system has been studied in detail in the presence of the heteropolyanions  $\text{XM}_{12}\text{O}_{40}^{z-}$  and  $\text{X}_2\text{M}_{18}\text{O}_{62}^{z-}$  and isopolyanions  $\text{M}_x\text{O}_y^{z-}$  ( $\text{M} = \text{Mo}^{6+}$  or  $\text{W}^{6+}$ ;  $\text{X} = \text{P}^{5+}$ ,  $\text{Si}^{4+}$  or  $\text{B}^{3+}$ ) as precursors of catalytically active peroxopolyoxometalates. The anions  $\text{BW}_{12}\text{O}_{40}^{5-}$ ,  $\text{SiW}_{12}\text{O}_{40}^{4-}$ , and  $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$  are inactive and, as shown by a number of spectroscopic methods, do not change their structure during the reaction.  $\text{PMo}_{12}\text{O}_{40}^{3-}$  exhibits a low activity. On the other hand,  $\text{PW}_{12}\text{O}_{40}^{3-}$  exhibits a high activity (79% yield of epoxide based on 1-octene) when the catalytic system is prepared beforehand by the reaction of the heteropolyanion with  $\text{H}_2\text{O}_2$  in aqueous solution in the absence of  $\text{Q}^+$  and 1-octene. When all the reagents are mixed simultaneously, no activity is observed. Tungstic acid, " $\text{H}_2\text{WO}_4$ ," and  $\text{H}_2\text{W}_{12}\text{O}_{42}^{10-}$  show high activities regardless of the preparation method used, the yields being 76% and 67%, respectively. The Keggin heteropolyanions are decomposed by the interaction with excess  $\text{H}_2\text{O}_2$   $\{[\text{H}_2\text{O}_2]/[\text{M}] = 30\text{--}355 \text{ mol/mol}\}$  to form the peroxopolyoxometalates  $\text{PM}_4\text{O}_{24}^{3-}$  and  $\text{M}_2\text{O}_{11}(\text{H}_2\text{O})_2^{2-}$ . It has been suggested that  $\text{PM}_4\text{O}_{24}^{3-}$  is the active species responsible for the olefin epoxidation with the Keggin anions  $\text{PM}_{12}\text{O}_{40}^{3-}$  in two-phase systems [146].

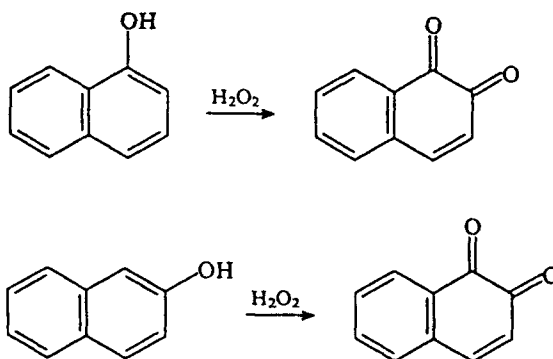
However, the recently reported  $^{31}\text{P}$  and  $^{183}\text{W}$  NMR study [147] gives evidence for the formation of peroxotungstophosphates,  $\text{PW}_x\text{O}_y^{z-}$  ( $x = 1\text{--}4$ ), in the aqueous  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{H}_2\text{O}_2$  system, which may well be the active species or their precursors in the olefin epoxidation by phase transfer catalysis. The novel  $\text{HPW}_2\text{O}_{14}^{2-}$  anion has been studied in the crystalline state and in solution. The crystal structure of  $[(n\text{-Bu})_4\text{N}]_2[\text{HPW}_2\text{O}_{14}]$  is closely related to that of  $[(n\text{-Bu})_4\text{N}]_3[\text{PW}_4\text{O}_{24}]$  (Fig. 11). The two anions,  $\text{HPW}_2\text{O}_{14}^{2-}$  and  $\text{PW}_4\text{O}_{24}^{3-}$ , include the  $[\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2]$  moiety as a principal building block. In a two-phase epoxidation of limonene by  $\text{H}_2\text{O}_2$ , tungsten species  $\text{Q}_3[\text{PW}_4\text{O}_{24}]$  and  $\text{Q}_2[\text{HPW}_2\text{O}_{14}]$ , proved to be 30 times more active than the molybdenum analog,  $\text{Q}_3[\text{PMo}_4\text{O}_{24}]$ .

Unlike  $\text{PW}_{12}\text{O}_{40}^{3-}$ , the  $[\text{Fe}_4(\text{PW}_9\text{O}_{34})_2]^{10-}$  anion was reported to be quite stable with respect to solvolysis by  $\text{H}_2\text{O}_2$ ; it catalyzed the selective homogeneous epoxidation of alkenes in aqueous acetonitrile at  $20^\circ\text{C}$  by  $\text{H}_2\text{O}_2$  [148].

Ishii et al. [142, 149–154] have extensively studied the oxidation by hydrogen peroxide with heteropolyoxometalate catalysts having a phase-transfer function. Thus cetylpyridinium salts of  $\text{PW}_{12}\text{O}_{40}^{3-}$  and  $\text{PW}_4\text{O}_{24}^{3-}$ , which can be easily prepared by treating  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{H}_2\text{O}$  or  $\text{H}_3\text{PW}_{12}\text{O}_{40}/35\% \text{H}_2\text{O}_2$ , respectively, with cetylpyridinium chloride in water, have been found to be versatile catalysts for a wide variety of oxidations by  $\text{H}_2\text{O}_2$  such as epoxidation of olefins [142], oxidative cleavage of olefins and *vic*-diols [149, 152], ketonization of alcohols and diols [149, 152], conversion of alkynes into  $\alpha,\beta$ -epoxy ketones [150], and oxidation of  $\alpha,\beta$ -unsaturated carbonyl

compounds [153], aliphatic and aromatic amines [151, 154], etc. These reactions proceed under mild conditions and often with very high selectivities.

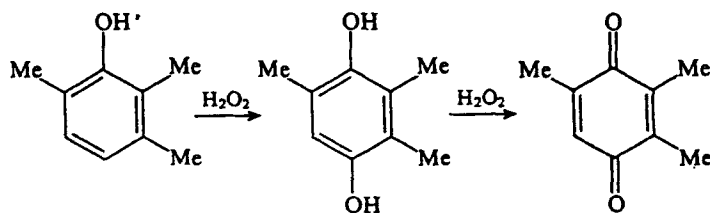
$\alpha$ - and  $\beta$ -Naphthols ( $10^{-3}$  M) are oxidized by  $\text{H}_2\text{O}_2$  (2–15%) to 1,2-naphthoquinone in 80–98% yield at  $20^\circ\text{C}$  in the 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ - $\text{H}_2\text{O}$  system in the presence of peroxoheteropolytungstates and trioctylbenzylammonium chloride (TOBAC). When the naphthol concentration is increased, C—C



coupling products are formed. The catalytic system is prepared by mixing  $\text{PO}_4^{3-}$ ,  $\text{WO}_4^{2-}$ , and TOBAC in molar ratio of 8:4:3.  $\text{PW}_4\text{O}_{24}^{3-}$  is suggested to be the active form of the catalyst. The ESR spectra give evidence that the reaction proceeds via the intermediate formation of semiquinone radicals [155].

Styrene–butadiene and isobutene–isoprene copolymers are epoxidized by hydrogen peroxide in the presence of  $\text{PW}_{12}\text{O}_{40}^{3-}$  [156].

The Keggin heteropoly acids catalyze the oxidation of 2,3,5- and 2,3,6-trimethylphenol (TMP) to 2,3,5-trimethyl-1,4-benzoquinone (TMBQ) by hydrogen peroxide in acetic acid solution in 65–78% selectivity at 94–100% TMP conversion [157]. The mechanism proposed involves the HPA-cata-



lyzed hydroxylation of the benzene ring to form 2,3,5-trimethylhydroquinone, followed by its fast oxidation to TMBQ. In this reaction, HPAs apparently behave as Brönsted acid catalysts. TMP is oxidized similarly by hydrogen peroxide in  $\text{H}_2\text{SO}_4$ - $\text{AcOH}$  [158]. It was shown that in acetic acid

solution in the presence of a strong mineral acid,  $\text{H}_2\text{O}_2$  is rapidly converted into peracetic acid, which is probably the true hydroxylating species [159].

The molybdovanadium isopolyacids  $\text{H}_2\text{V}_{12-x}\text{Mo}_x\text{O}_{31}$  ( $x = 0-4$ ) catalyze the oxidation of 1,2,4-trimethylbenzene to TMBQ by peracetic acid in acetic acid solution (20°C, 4 h) with a 12–31% selectivity at 15–22% trimethylbenzene conversion [160].

The oxidation of ethylbenzene by hydrogen peroxide in acetonitrile in the presence of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ , and their tetrabutylammonium salts gives acetophenone as the main product (100% selectivity and 5–17% PhEt conversion) [161].

### C. Oxidation with Organic Peroxides

The epoxidation of 1-hexene by cumyl hydroperoxide (CHP) in isopropanol catalyzed by HPA salts at 110°C proceeds with a 100% selectivity and >80% CHP conversion. The reaction rate is described by the kinetic equation  $w = k[\text{HPAN}]^p[\text{CHP}][\text{C}_6\text{H}_{12}]$ , where  $p = 0.5-0.9$  for  $[\text{HPAN}] = (0.2-9) \cdot 10^{-5}$  M. The catalytic activity of HPA salts decreases in the series:  $\text{Na}_3\text{PMo}_{12}\text{O}_{40} = \text{AlPMo}_{12}\text{O}_{40} > \text{Na}_4\text{PMo}_{11}\text{VO}_{40} > \text{Na}_4\text{SiMo}_{12}\text{O}_{40} \gg \text{Na}_3\text{PW}_{12}\text{O}_{40}$ . The HPAs themselves are not effective in the epoxidation because they catalyze the decomposition of CHP to phenol and acetone [100]. The reaction mechanism is suggested to involve the decomposition of the heteropolyanion with the formation of monomeric Mo(VI) complexes, which are probably the catalytically active species [162].

$[(n\text{-Bu}_4\text{N})_4\text{H}]\text{PW}_{11}\text{O}_{39}\text{M}$ , where  $\text{M} = \text{Mn(II)}, \text{Co(II)}, \text{Cu(II)}, \text{Fe(II)}$ , etc., catalyze the oxidation of cyclohexanol and adamantane by *t*-butyl hydroperoxide (TBHP) in benzene. The selectivity to oxidation products (cyclohexanol or 1-adamantanol, 2-adamantanol and 2-adamantanone) reaches 90% based on TBHP consumed. Such metal-substituted polyoxometalates also catalyze the oxidation of olefins (cyclohexene, 1-hexene, norbornene, and cyclooctene) by iodosobenzene and pentafluoriodosobenzene in acetonitrile, the Mn(II) and Co(II) complexes exhibiting the highest activity [163, 164].

$[(\text{C}_6\text{H}_{13})_4\text{N}]_5\text{SiW}_{11}\text{O}_{39}\text{Ru}(\text{H}_2\text{O})$  catalyzes the liquid-phase oxidation of alkanes and alkenes by TBHP as well as by potassium persulfate, sodium periodate, and iodosobenzene [165].

### D. Miscellaneous Oxidation

Primary alcohols and aldehydes are readily oxidized to carboxylic acids in a 100% yield by  $\text{KClO}_3$  in aqueous solution (pH 2, 25–75°C) in the presence of a catalytic system prepared by the interaction of  $\text{K}_2\text{RuOHCl}_5$  with  $\text{Na}_7\text{PW}_{11}\text{O}_{39}$  [166].

#### IV. CONCLUDING REMARKS

The selected examples reviewed show the broad scope of promising applications of HPA catalysis in low-temperature liquid-phase organic reactions, in particular in the synthesis of fine chemicals. Generally, HPAs provide higher activities and selectivities and allow for cleaner processing. The high effectiveness of HPAs as acid catalysts is primarily due to their strong Brønsted acidity, which exceeds the acidity of ordinary mineral acids and conventional solid-acid catalysts. This makes it possible to carry out the catalytic process at a lower catalyst concentration and/or a lower temperature. The efficient operation under milder conditions generally provides the gain in reaction selectivity. Furthermore, by virtue of their inertness towards organic substrates, HPAs are incapable of participating in side reactions such as sulfonation, chlorination, nitration, etc., which are typical of mineral acids. HPAs can be used as homogeneous or heterogeneous (bulk and supported) catalysts. The heterogeneous HPA catalysts can be readily recovered from the reaction products without neutralization and reused. In the homogeneous systems, although the neutralization of HPAs is usually necessary, the amount of alkali needed and hence the amount of wastes formed thereupon is much less than with mineral acids. In some cases, e.g., in polymerization of tetrahydrofuran [2, 3] and esterification of *p*-nitrobenzoic acid [5], when two-phase systems are formed in the course of homogeneous reaction, the recycling of HPAs can be done without neutralization. In liquid-phase oxidation, polyoxometalates can be applied profitably either as stoichiometric oxidants or as catalysts in conjunction with such terminal oxidants as O<sub>2</sub>, H<sub>2</sub>O, organic peroxides, etc. The application of a variety of two-component redox systems based on polyoxometalates greatly extends the scope of possible oxidations. As regards practical applications of HPA catalysis, the search for new and more efficient catalytic reactions, the design of more effective and more stable HPA catalysts, the development of advanced methods for the preparation of HPAs, and the improvement of methods of catalyst recovery and recycling, etc., are of current interest.

#### V. SUMMARY

Catalysis with heteropoly acids (HPA) and related polyoxometalate systems is a field of growing importance. Recently, new large-scale industrial processes based on HPA catalysis such as oxidation of methacrolein, hydration of olefins, and polymerization of tetrahydrofuran have been developed and commercialized. The purpose of this review is to discuss the use of HPAs as acid and oxidation catalysts for low-temperature liquid-phase organic reactions. A wide variety of syntheses of antioxidants, medicines, vitamins, and other fine chemicals based on HPA catalysis in ho-

mogeneous and heterogeneous liquid-phase systems are reviewed. An outline of HPA acid and redox properties, new methods of HPA preparation, catalyst characterization, and mechanistic aspects of HPA catalysis is also given. Under discussion are the following reactions: alkylation, dealkylation, and transalkylation of phenols; condensation (syntheses of vitamins E, K<sub>1</sub>, and C); hydration and dehydration reactions; esterification and etherification; oxidation of olefins, arenes, and phenols with O<sub>2</sub>; oxidations with H<sub>2</sub>O<sub>2</sub>; etc. The examples reviewed show the broad scope of promising applications of HPA catalysis for low-temperature organic reactions, in particular for fine chemical synthesis.

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