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Catalysis by Heteropoly Acids and Multicomponent Polyoxometalates in Liquid-Phase Reactions

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Contents

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I. Introduction

Catalysis by heteropoly acids (HPAs) and related polyoxometalate compounds is a field of increasing importance.[1−16] HPAs have several advantages as catalysts which make them economically and environmentally attractive. On the one hand, HPAs have a very strong, approaching the superacid region, Brönsted acidity; on the other, they are efficient oxidants, exhibiting fast reversible multielectron redox transformations under rather mild conditions. Their acid−base and redox properties can be varied over a wide range by changing the chemical composition. Solid HPAs possess a discrete ionic structure, comprising fairly mobile basic structural units—heteropolyanions and countercations (H^+, H_3O^+, $H_5O_2^+$, etc.)—unlike the network structure of, e.g., zeolites and metal oxides. This unique structure manifests itself to exhibit an extremely high proton mobility and a “pseudoliquid phase”[8] (see later), while heteropolyanions can stabilize cationic organic intermediates.[11] On top of that, HPAs have a very high solubility in polar solvents and fairly high thermal stability in the solid state. These properties render HPAs potentially promising acid, redox, and bifunctional catalysts in homogeneous as well as in heterogeneous systems. HPAs are widely used as model systems for fundamental research, providing

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unique opportunities for mechanistic studies on the molecular level. At the same time, they become increasingly important for applied catalysis. Most of the pioneering work has been done since the 1970s mainly by Japanese and Russian reasearch groups.[1−3,8,11] 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.[2−16] Several new industrial processes based on HPA catalysis, such as oxidation of methacrolein, hydration of olefins (propene and butenes), polymerization of tetrahydrofuran, etc., have been developed and commercialized.[10]

The purpose of this review is to discuss the scope and limitations of HPAs as acid and oxidation catalysts for liquid-phase organic reactions in homogeneous and heterogeneous systems. Such topics as HPA acid and redox properties, catalyst preparation and characterization, and mechanistic aspects of HPA catalysis are also surveyed. The review mainly covers the recent literature published during the past five years, although, for a more comprehensive discussion, some earlier works are also included. More detailed information about the preparation of HPAs and their physicochemical properties can be found in monographs and reviews[14,17−23] and other articles in this issue. A series of reviews, discussing various aspects of HPA catalysis have been published.[1−16]

II. Acid Catalysis by Heteropoly Acids

A. HPA Catalysts

1. Structure

Molecular Structure. HPAs are complex proton acids that incorporate polyoxometalate anions (heteropolyanions) having metal−oxygen octahedra as the basic structural units.[17−24] The first characterized and the best known of these is the Keggin heteropolyanion typically represented by the formula $XM_{12}O_{40}^{x-8}$ where X is the central atom (Si^{4+}, P^{5+}, etc.), *x* is its oxidation state, and M is the metal ion (Mo^{6+}or W^{6+}). The M^{6+} ions can be substituted by many other metal ions, e.g., V^{5+}, Co^{2+}, Zn^{2+}, etc. The Keggin anion is composed of a central tetrahedron XO_4 surrounded by 12 edge- and corner-sharing metal−oxygen octahedra MO_6 (Figure 1).[24] The octahedra are arranged in four M_3O_{13} groups. Each group is formed by three octahedra sharing edges and having a common oxygen atom which is also shared with the central tetrahedron XO_4. Among a wide variety of HPAs, the Keggin's are the most stable and more easily available; these are the most important for catalysis. In this review HPAs are understood as the Keggin acids, unless otherwise stated. Generally, their formulas will be abbreviated to XM, e.g., PW and SiW for $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, respectively. Other polyoxometalates—e.g., those of the Dawson structure, $X_2M_{18}O_{62}^{2x-16}$; Keggin and Dawson lacunary anions, $XM_{11}O_{39}^{x-12}$ and $X_2M_{17}O_{61}^{2x-20}$; and transition metal complexes thereof[14,19]—are also used as catalysts.

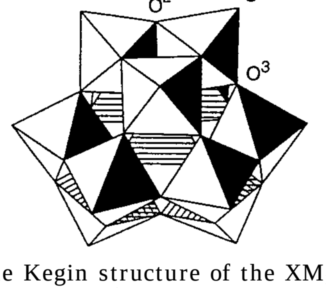


Figure 1. The Kegin structure of the $XM_{12}O_{40}^{x-8}$ anion (α-isomer):[24] terminal (O^1), edge-bridging (O^2), and corner-bridging (O^3) oxygen atoms.

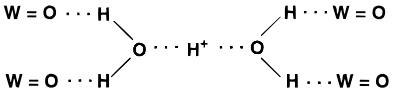


Figure 2. The schematic structure of bulk proton sites in $H_3PW_{12}O_{40}·6H_2O$.[28]

Generally, solid HPAs form ionic crystals composed of heteropolyanions, countercations (H^+, H_3O^+, $H_5O_2^+$, etc.) and hydration water. The crystal structure of HPAs depends on the amount of hydration water.[17−23] This water can be easily removed on heating, whereby the acid strength is increased due to the dehydration of protons. This is a reversible process accompanied by changing the volume of crystal cell. Unlike the rigid network structure of zeolites, in HPA crystal the Keggin anions are quite mobile. Not only water but also a variety of polar organic molecules can enter and leave HPA crystal. Such structural flexibility is important when using HPA as a heterogeneous catalyst (see below).[8,11]

Proton Structure. HPAs are strong Brönsted acids.[2,4,8,11] Structural characterization of the HPA proton sites is an important step toward understanding the catalytic activity.[4,8,25] Keggin anions have three types of outer oxygen atoms as potential protonation centers: terminal oxygens M═O and two types of bridging oxygens M—O—M, edge sharing and corner sharing (Figure 1). Bond length−bond strength correlations[26] as well as ^{17}O nuclear magnetic resonance (NMR) data[27] indicate that in the free polyanions (e.g., $V_{10}O_{28}^{6-}$) in solution, the bridging oxygen atoms, having a higher electron density than the terminal oxygen atoms, are protonated. Hypothetically, in the free Keggin anion in the gas phase, edge-bridging M−O−M oxygens may be assumed to be the predominant protonation sites. In solid HPAs, the protons take part in the formation of the HPA crystal structure, linking the neighboring heteropolyanions. In this case the more accessible terminal oxygens can be protonated. Thus, from single-crystal X-ray and neutron diffraction data,[28] the crystal structure of PW hexahydrate is formed by packing heteropolyanions into a body-centered cubic structure. The bulk proton sites in PW hexahydrate are represented as diaquahydrogen ions, $H_5O_2^+$, each of which links four neighboring heteropolyanions by forming hydrogen bonds with the terminal W═O oxygens (Figure 2). Note, however, that the protons cannot be found directly from X-ray data; their positions are localized on the basis of a sensible hydrogen-bonding scheme and the known geometry of the water molecule.

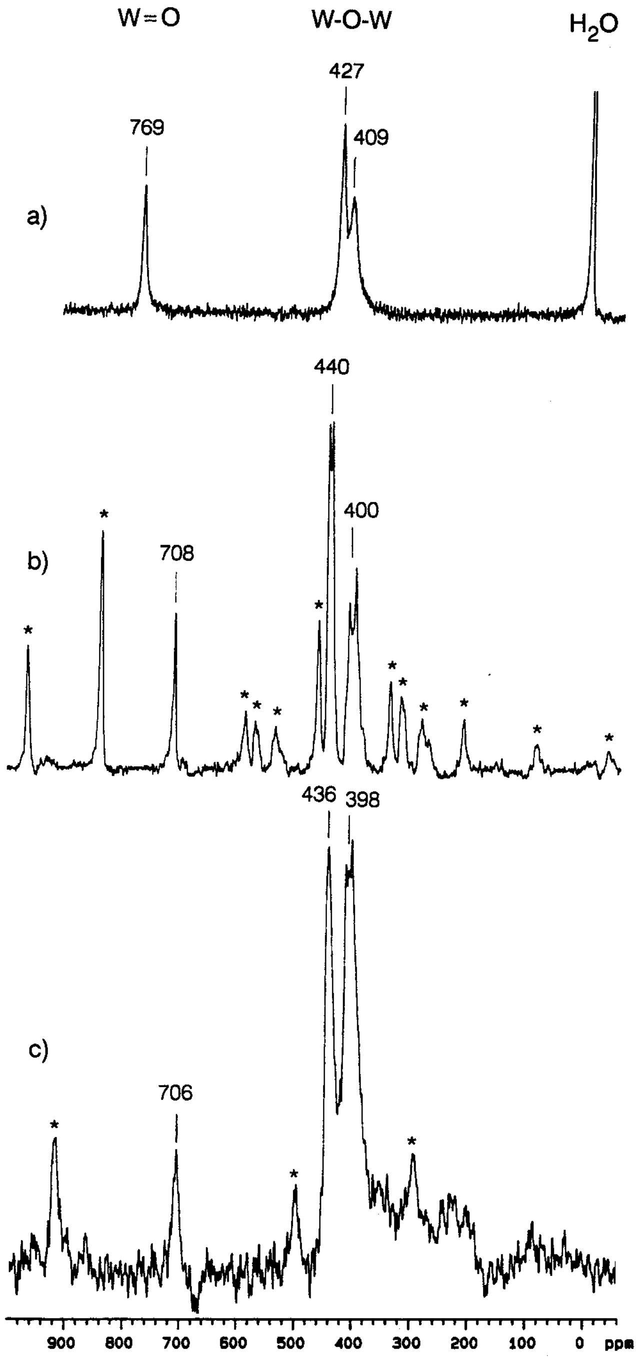


Figure 3. ^{17}O NMR spectra for ^{17}O-enriched PW: (a) 0.12 M PW aqueous solution; and (b and c) magic-angle spinning spectra for solid PW at a spinning rate of 6.8 and 11 kHz, respectively; positions of center bands are indicated; spinning side bands are asterisked.[30]

Direct evidence of the predominant protonation of the terminal oxygens in solid PW and SiW has been obtained by ^{17}O NMR by comparison of solution and solid-state spectra for these HPAs.[29-32] The resonance for the terminal oxygen in solid PW exhibits a large 60 ppm upfield shift compared to the aqueous solution spectrum, whereas the bridging oxygen resonances have practically the same positions in both spectra (Figure 3).[29-31] Since in aqueous solution PW is completely deprotonated (see below), this unambiguously identifies the terminal oxygens as the predominant protonation sites in solid HPA. The structure of proton sites in the dehydrated PW is shown in Figure 4. 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 equivalent terminal oxygens, belonging to four different heteropolyanions, like in PW hexahydrate. Interestingly, the same structure was suggested[28] for the structurally similar HPA salts, e.g., $Cs_3PW_{12}O_{40}$, in which the Cs^+ ions each have four equivalent terminal oxygens as the closest neighbors.

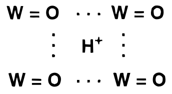


Figure 4. The schematic structure of bulk proton sites in dehydrated PW.[30]

2. Acid Properties

HPA in Solution. In solutions, the acid properties of HPAs are quite well documented in terms of dissociation constants and Hammett acidity function.[2,4] HPAs have very high solubilities in polar solvents such as water, lower alcohols, ketones, ethers, esters, etc. On the other hand, they are insoluble in nonpolar solvents like, e.g., hydrocarbons. The dissociation constants of HPAs were measured in such solvents as H_2O,[33] Me_2CO, EtOH, and AcOH,[34] etc.; the Hammett acidity function was determined in H_2O and $H_2O-AcOH$, H_2O-dioxane, $H_2O-EtOH$, and H_2O-Me_2CO mixtures.[35] The stability of HPAs toward hydrolysis in aqueous solution follows the order: SiW > PW > SiMo > PMo.[17,36]

In aqueous solution, HPAs such as PW, SiW, and PMo are strong fully dissociated acids.[4] $SiW_{12}O_{40}{}^{4-}$ and $PW_{12}O_{40}{}^{3-}$ anions remain deprotonated even after accepting two and three extra electrons, respectively, upon polarographic reduction in aqueous solution at pH 1.[37] From ^{17}O NMR data,[31] PW remains fully ionized in a 94:6 v/v $AcOH-H_2O$ solution, the solvated protons loosely bound to the anion as a whole rather than to a certain oxygen atom in the anion. HPAs in solution are stronger than the usual mineral acids such as H_2SO_4, HCl, HNO_3, etc. (Table 1). The strength of the Keggin HPAs depends weakly on their composition. Yet the tungsten acids are markedly stronger than molybdenum ones. The strongest 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 stronger than that of equimolar solutions of H_2SO_4.[4]

Although the acid strength and catalytic activity of Brönsted acids are best quantified in terms of their

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

acid	pK_1	pK_2	pK_3
$H_3PW_{12}O_{40}$	1.6	3.0	4.0
$H_4PW_{11}VO_{40}$	1.8	3.2	4.4
$H_4SiW_{12}O_{40}$	2.0	3.6	5.3
$H_3PMo_{12}O_{40}$	2.0	3.6	5.3
$H_4SiMo_{12}O_{40}$	2.1	3.9	5.9
H_2SO_4	6.6		
HCl	4.3		
HNO_3	9.4		

Table 2. Sorption of Different Substances onto PW at 25 °C[46]

substance	sorption (molecules per Keggin unit) irreversible[a]	total
pyridine	6.0	9
ammonia	3.2	4.3
methanol	2.2	>10
isopropyl alcohol	6.3	>10
ethylene	0.03	0.04
1-butene	0.2	0.25
benzene	0.1	0.5

[a] The amount irreversibly retained after evacuation at 25 °C.

dissociation constants and Hammett acidity function, other characteristics, namely the hardness of the acid or the softness of the corresponding base have also been used. These are the key parameters of the hard and soft acid−base theory related to the polarizabilities of the acids and bases and generally applied to Lewis acids and bases.[38] According to Izumi et al.,[39] Keggin anions can be characterized as having a very weak basicity and great softness. The order of softness of heteropolyanions in aqueous solution was estimated as follows: $SiW_{12}O_{40}^{4-} > GeW_{12}O_{40}^{4-} > PW_{12}O_{40}^{3-} > PMo_{12}O_{40}^{3-} > SiMo_{12}O_{40}^{4-} > NO_3^- > TsO^- > SO_4^{2-}$.

The softness of heteropolyanions is assumed to play an important role in stabilizing organic intermediates.[11]

Solid HPAs possess purely Brönsted acidity and are stronger than such conventional solid acids as $SiO_2-Al_2O_3$, H_3PO_4/SiO_2, and HX and HY zeolites.[40,41] The acid strength of crystalline HPAs decreases in the series PW > SiW ≥ PMo > SiMo which is identical to that in solutions (Table 1).[4,8] Usually, relative catalytic activities of HPAs are consistent with this order both in homogeneous and in heterogeneous systems.[4,8] Like other strong solid acids, HPAs are capable of generating carbocations from adsorbed olefins and arenes.[42]

HPAs have a fairly high thermal stability. The Keggin-type PW, SiW, PMo, and SiMo decompose at 465, 445, 375, and 350 °C, respectively.[43] The decomposition causes the loss of their acidity. However, thermally decomposed molybdenum HPAs become reconstructed under exposure to water vapor.[44,45] Under wet conditions, molybdenum HPAs can hence be used as solid acid catalysts in vapor-phase reactions operated at relatively high temperatures. In the case of much less labile tungsten HPAs such reconstruction seems unlikely.

Misono et al.[8,12] demonstrated that crystalline HPAs in many respects behave like solutions. This is due to the fact that these solids have discrete and mobile ionic structures. Solid HPAs absorb a large amount of polar molecules, e.g., alcohols, ethers, amines, etc., in the catalyst bulk, forming HPA solvates[46] (Table 2). Moreover, solid HPAs possess an extremely high proton mobility. It should be noted that proton conductivities of solids generally correlate with their acid−base catalytic activities.[47] The mechanism of the proton conductivity of solid HPAs has been discussed.[47]

By virtue of the easy absorption, polar molecules undergo catalytic reactions not only on the surface, but also in the bulk of the crystalline HPA. Thus, toward polar substances, solid HPAs behave like highly concentrated solutions, i.e., nearly 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”.[8] Unlike polar molecules, nonpolar reactants (e.g., hydrocarbons) are incapable of being absorbed in the HPA bulk (Table 2). They interact only with the surface of the catalyst. The pseudoliquid behavior apparently brings about high catalytic activities for reactions of polar molecules at relatively low temperatures, i.e., when the sorption of the substrate in the catalyst bulk is rather high. Besides the activities, unique selectivities have been reported.[8] On top of that, the uniformity of pseudoliquid phase makes it feasible to use spectroscopic techniques to study the catalytic process.[48]

According to microcalorimetric data,[49] the bulk proton sites in dehydrated PW are essentially uniform, which is not unexpected due to the pseudoliquid behavior of HPA. These 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. Other microcalorimetric studies[50,51] have examined the acid strengths of a number of HPAs by the sorption of NH_3 after pretreatment of the solids under various conditions. An effect of activation conditions was observed in that a lower activation temperature resulted in a higher differential heat of sorption. The order of acid strengths of solid HPAs, as determined by microcalorimetry at a sorption temperature of 50 °C after pretreatment at 150 °C, is PW ≥ SiW >> PMo ≥ SiMo, which is in agreement with that found by temperature-programmed desorption (TPD).[50]

Solid PW and its acidic salt $Cs_{2.5}H_{0.5}PW$ after pretreatment at 300−400 °C have been claimed to acquire superacid sites.[52−54] (By definition,[55] superacids are acids stronger than 100% H_2SO_4; they have the Hammett acidity function H_o less than −12). Thus, Okuhara et al.[53] showed by titration with Hammett indicators that the calcined PW and $Cs_{2.5}H_{0.5}PW$ have the acid sites with $H_o < -13.16$. However, the application of Hammett indicators to characterize the surface acidity of solid acids can be misleading because the surface acidity function H_o, in contrast to the solution H_o, does not have an explicit physicochemical meaning (for a recent review, see ref 15). Another useful yet not sufficient criterion to identify superacids is based on their catalytic activity: superacids are capable of catalyzing the low-temperature (below 100 °C) skeletal isomerization of light alkanes.[55] According to this criterion, neither PW nor $Cs_{2.5}H_{0.5}PW$ can be regarded as superacids because they catalyze *n*-butane isomerization only at about 300 °C.[54] Nowinska et al.[52] reported that bulk and SiO_2-supported PW show a very low catalytic activity in the skeletal isomerization of *n*-hexane at 75 °C. Apparently, solid HPAs are to be considered as very strong, approaching the superacidity region, Brönsted acids.

3. Supported HPAs

Supported HPA catalysts are important for applications because bulk HPAs have a low specific surface (1−5 $m^2 g^{-1}$).[2,4,8,11] A variety of methods have been used to characterize such catalysts,[8,11,15] multinuclear solid-state NMR being particularly useful probe of the state of HPA.[56−62] The acidity and 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 SiO_2,[63] active carbon,[64,65] acidic ion-exchange resin,[66] etc., are suitable as supports, the most often used being SiO_2. Basic solids like MgO tend to decompose HPA.[4,8,67]

HPA on Silica. SiO_2 is relatively inert toward HPAs, at least above a certain loading level, although some chemical interaction takes place between HPA and SiO_2 (see below). The thermal stability of HPA on SiO_2 seems to be comparable to or slightly lower than that of the parent HPA.[8,68] On the other hand, a thermally decomposed Keggin structure on the silica surface may be reconstructed on exposure to water vapor.[45,69]

^1H and ^{31}P magic-angle spinning (MAS) NMR studies indicate a chemical interaction of PW with SiO_2.[57,58,60,70] Impregnating SiO_2 with an aqueous solution of PW gives catalysts with, in general, two HPA species which were characterized by ^{31}P MAS NMR: one at −15 ppm with intact Keggin structure (A) and the other at −14 ppm with a different structure (B) (Figure 5).[60,70] The relative amount of species A and B depends on HPA loading, with A dominating. At higher loadings, 30−50%, A is practically the only one present on the SiO_2 surface; at lower loadings, both species exist, the amount of B increasing as the HPA loading decreases. In contrast, catalysts prepared by impregnation with a methanol solution of HPA contain exclusively Keggin-type A over the whole range of PW loading.[70] Forms A and B were assumed to be bulk crystalline PW and the "interacting" species $(SiOH_2^+)(H_2PW_{12}O_{40}^-)$, respectively.[60] More recently evidence was obtained that B may be $H_6P_2W_{18}O_{62}$ or $H_6P_2W_{21}O_{71}$, formed from PW in the course of catalyst preparation.[70] The B species was more active than A in liquid-phase dealkylation of alkylphenols.[70] The ^1H MAS NMR study[57] also shows the interaction of PW with silica and the formation of a new type of proton sites on the silica surface.

As shown by microcalorimetry,[49] when loading PW (20 wt %) on SiO_2, the proton sites become weaker and less uniform. Only 20% of the total amount of proton sites remain as strong as in bulk PW. The rest has the differential heat of ammonia adsorption about 120 kJ/mol, approaching that for acid sites of HX and HY zeolites. Like for bulk HPA, the differential heat of NH_3 adsorption on SiO_2-supported HPA strongly depends on the pretreatment temperature.[51] According to the ammonia thermal desorption data,[49] the acid strength of supported PW decreases in the series of carriers: $SiO_2 > \alpha\text{-}Al_2O_3 >$ activated carbon.

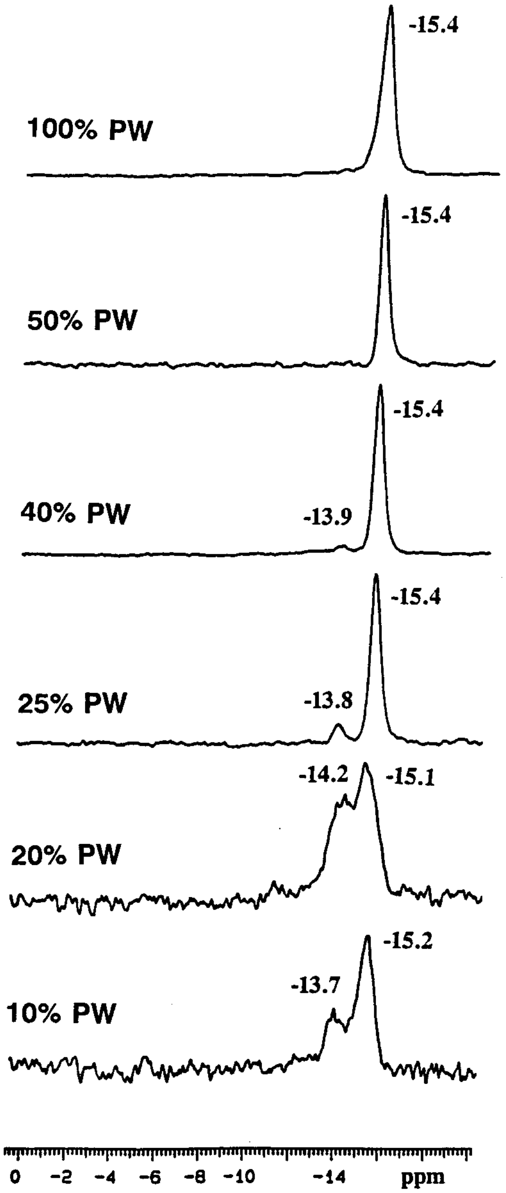


Figure 5. ^{31}P MAS NMR spectra for PW and PW/SiO_2 at various PW loadings.[70]

At low loadings, PW and SiW form finely dispersed species on the SiO_2 surface; HPA crystal phase on silica (200−300 $m^2 g^{-1}$) is developed at HPA loading above 20 wt %.[63,71] Various HPA forms were observed on the silica surface by transmission electron microscopy (TEM): discrete molecules, clusters 50 Å in size and large crystallites of 500 Å. Their relative amounts depend on the HPA loading.[71]

SiO_2-supported molybdenum HPAs, such as SiMo, PMo, and $PMo_{10}V_2$, retain the Keggin structure at high loadings but decompose at very low loadings due to their strong interactions with surface silanol groups.[45,68,72−74] 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.[68,72,74] At high loadings, supported HPAs behave similarly to bulk HPAs. In this case, acid catalysis predominates to yield dim-

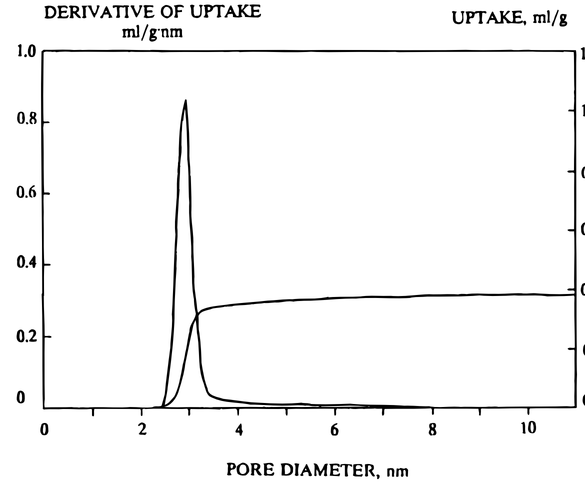


Figure 6. Pore size distribution for 40% PW/MCM-41 (from N_2 physisorption).[76]

ethyl ether. In contrast, at low loadings, when HPA decomposes to MoO_3, losing the acidity, only redox catalysis is observed to give formaldehyde.

HPA on Mesoporous Molecular Sieve. Incorporation of HPA into zeolite pores to obtain shape-selective catalysts has long been a challenge. However, conventional zeolites are not suitable for this because their pores are too small to adsorb large (12 Å) HPA molecules. Recently, PW supported on a novel mesoporous pure-silica molecular sieve MCM-41 (BET surface area 1200 $m^2\ g^{-1}$, uniform pores 32 Å in size) was prepared[75,76] and characterized by nitrogen physisorption, XRD, Fourier-transform infrared spectroscopy (FT-IR), TEM, and ^{31}P MAS NMR.[70,75] The PW/MCM-41 compositions with PW loadings from 10 to 50 wt % have ~30 Å uniformly sized mesopores (Figure 6). 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, as in the case of amorphous SiO_2.[70] HPA forms finely dispersed species on the MCM-41 surface. No HPA crystal phase is seen at HPA loadings as high as 50 wt %. As shown by TEM,[70] the PW species are mainly located inside the MCM-41 pores rather than on the outer surface (Figure 7). PW/MCM-41 exhibits a higher catalytic activity than H_2SO_4 or bulk PW and shows a shape selectivity in liquid-phase phenol alkylation.[75] SiW/MCM-41 has been characterized and tested in the esterification of acetic acid with *n*-butyl alcohol.[77] This catalysts is very similar to PW/MCM-41.

The encapsulation of PW in the cage of synthetic faujasite has been claimed,[78] however, more characterization is needed to prove it; no preparation details has been disclosed.

HPA on Carbon. 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 toward HPA leaching from the carrier.[64,65] However, as shown by microcalorimetry,[79] the acid strength of PW is greatly reduced when loading on activated carbon. As evidenced by IR and ^{31}P MAS NMR, PW and SiW supported on a chemically (H_3PO_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 the HPA loading as high as 45 wt %.[30] In ^{31}P MAS NMR spectra of carbon-supported PW, a great line broadening was observed due to a strong interaction of the HPA with carbon.[30] Carbon-supported $H_{3+n}PMo_{12-n}V_nO_{40}$ as catalysts for liquid-phase oxidation have been studied.[80,81] Scanning tunneling microscopy and tunneling spectroscopy studies on HPAs supported on graphite have been reported.[82,83]

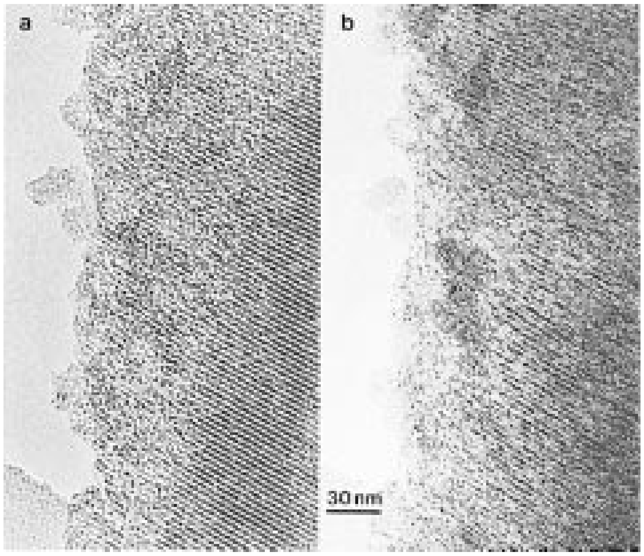


Figure 7. TEM images of the same area of 40% PW/MCM-41: (a) before and (b) after amorphization. The same structure observed before and after amorphization is a clear indication that HPA is mainly located inside the MCM-41 pores. (Reprinted from ref 70. Copyright Elsevier Science B.V.)

Other Supported HPA Catalysts. Pillaring hydrotalcite-type anionic clays (layered double hydroxides) by polyanions to form expanded layered catalysts for redox reactions has attracted considerable interest. These materials are often used as precursors for molecularly mixed oxide catalysts, which possess basic and/or redox properties.[84] Pillared layered double hydroxides have been prepared by ion-exchange reaction of $[Zn_2Al(OH)_6]NO_3xH_2O$ with the Keggin-type heteropolyanions.[85] Complete replacement of NO_3^- is achieved for Keggin anions, such as $PW_9V_3O_{40}^{6-}$, $H_2W_{12}O_{40}^{6-}$, $SiW_9V_3O_{40}^{7-}$, etc., with the charge of −6 or higher. No exchange was observed for anions such as $PW_{12}O_{40}^{3-}$ and $SiW_{12}O_{40}^{4-}$. The intercalated anions, below 200 °C, were accessible for catalytic chemical conversions, e.g., for photocatalytic oxidation of isopropyl alcohol to acetone. The intercalation of PW into a zinc aluminum carbonate hydroxide has been studied.[86] Upon interacting with the clay, PW was probably partially decomposed to form a highly dispersed PW_9 species, which, nevertheless, showed a higher catalytic activity and selectivity in dehydration of *n*-butyl alcohol than the bulk HPA at 230−250 °C. Recently the intercalation of a variety of transition metal-substituted polyoxometalates into ZnAl−NO_3 and MgAl−Cl host clays has been reported.[87,88] The pillaring of MgAl layered double hydroxides by $H_2W_{12}O_{40}^{6-}$,

$P_2W_{18}O_{62}^{6-}$, and $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ anions has been accomplished by ion exchange reaction.[89] Polyoxometalate-intercalated hydrotalcites showed catalytic activities for the liquid-phase oxidation of cyclohexene with O_2[90] and shape-selective epoxidation of alkenes with H_2O_2.[91]

HPA immobilized into an organic polymer, e.g., PMo−polysulfone, PMo−polyethersulfone,[92] PMo−polyacetylene[93], PMo−polypyrrole,[94] SiW−polyaniline,[95,96] and PMo− and PW−poly(1,4-phenylenemethylidynenitrilo-1,4-phenylenenitrilomethylidyne),[97] have been prepared and characterized. These are claimed to have an improved catalytic activity compared to bulk HPA in gas-phase ethanol conversion.

4. Salts of HPAs

The nature of countercation in HPA salts is critical with respect to their acidity, solubility, porosity, and thermal stability. Salts with rather small cations resemble the parent HPAs; they are readily soluble in water, nonporous, and possess surface areas under 10 m^2 g^{-1} (Table 3). In contrast, water-insoluble salts with large monovalent cations, such as NH_4^+, K^+, Cs^+, etc., have a rigid microporous/mesoporous structure and surface areas over 100 m^2 g^{-1}.[98] 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.[99] As demonstrated by Misono, Okuhara et al.,[54,100] acidic Cs salt, $Cs_{2.5}H_{0.5}PW$, has strong acid sites and high surface area (100−200 m^2 g^{-1}) and is an efficient solid acid catalyst for a variety of organic reactions, especially promising for liquid-phase reactions. The pore size of Cs salts $Cs_xH_{3-x}PW$ can be controlled by the Cs content. $Cs_{2.2}H_{0.8}PW$ possesses micropores of 6.2−7.5 Å diameter and exhibits shape-selective catalysis in a series of liquid-phase reactions.[101] Izumi et al.[102,103] reported that SiO_2-bound $Cs_{2.5}H_{0.5}PW$, prepared through the hydrolysis of ethyl orthosilicate in the presence of colloidal $Cs_{2.5}H_{0.5}PW$ in ethanol, is catalytically more active than Amberlyst-15 and H-ZSM-5, as based on the unit acid site. Catalysts obtained by loading HPAs on their insoluble salts, e.g., PMo/K_3PMo, have been studied.[104,105] Various methods of the preparation of bulk and supported HPA salts have been described.[106,107] The ^{129}Xe NMR method has been applied to characterize the pore structure of NH_4^+, K^+, and Cs^+ salts of PW, PMo, and SiW to confirm the presence of microporosity therein.[108]

Table 3. Physicochemical Properties of HPA Salts

cation	ionic radius, Å	solubility[a]	surface area, m^2 g^{-1}
Li^+	0.68	S	<10
Na^+	0.97	S	<10
Ag^+	1.26	S	<10
Mg^{2+}	0.66	S	<10
Ca^{2+}	0.99	S	<10
Cu^{2+}	0.72	S	<10
Zn^{2+}	0.74	S	<10
Al^{3+}	0.51	S	<10
Fe^{3+}	0.64	S	<10
La^{3+}	1.02	S	<10
Ce^{3+}	1.03	S	<10
K^+	1.33	N	>100
Rb^+	1.47	N	>100
Cs^+	1.67	N	>100
NH_4^+	1.43	N	>100

[a] Solubility in water: S, soluble; N, insoluble.

Certain "neutral" HPA salts can also gain proton sites upon the interaction with the reaction medium. Two mechanisms of the proton generation in heteropoly salts are distinguished: the dissociation of coordinated water (for salts with the cations like Al^{3+}, Zn^{2+}, etc.) and the reduction of the metal cation (for, e.g., Ag^+, Cu^{2+}, and Pd^{2+}).[2,8]

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+$$

$$Ag^+ + 1/2H_2 \rightarrow Ag^o + H^+$$

Ono et al.[2] have studied Pt(II) and Pd(II) salts of PW; these are capable of acting as bifunctional catalysts in alkane isomerization. ^{1}H NMR studies of protons in the catalysts consisting Pd^0 metal and PW show that the presence of H_2 and Pd^0 greatly modifies the dynamic nature of protons in PW.[109] Thus it was found that at 60 °C under H_2, the interconversion occurs between the hydrogen atoms on Pd^0 and protons in PW and that hydrogen atoms formed on Pd^0 spill over to the surrounding heteropolyanions. $Cs_{2.5}H_{0.5}PW$ catalyzes the *n*-butane isomerization to isobutane at 300 °C;[110] combining the Cs salt with noble metals such as Pt enhances the activity in the presence of H_2.[111]

B. Homogeneous Reactions

HPAs catalyze a wide variety of reactions in homogeneous liquid phase offering strong options for more efficient and cleaner processing compared to conventional mineral acids.[2−6,11,12] Being stronger acids, HPAs will have significantly higher catalytic activity than mineral acids. In particular in organic media, the molar catalytic activity of HPA is often 100−1000 times higher than that of H_2SO_4[4,12] (Table 4). This makes it possible to carry out the catalytic process at a lower catalyst concentration and/or at a lower temperature. Further, HPA catalysis lacks side reactions such as sulfonation, chlorination, nitration, etc., which occur with mineral acids.[4] As stable, relatively nontoxic crystalline substances, HPAs are also preferable with regard to safety and ease of handling.

Table 4. Homogeneous Reactions Catalyzed by HPA

reaction[a]	rate ratio[b]	*T* °C	ref
hydration of isobutene[c]	2−4	40	11
hydration of phenylacetylene	100	60	11
$PhC(CH_3)_2OOH \rightarrow PhOH + CH_3COCH_3$	1000	25	3
olefin + HOAc → ester	90	110	3
ester → olefin + carboxylic acid	100	128	112
$THF + Ac_2O \rightarrow AcO(CH_2CH_2CH_2CH_2O)_nAc$	>1000	50	11
styrene + HCHO (Prins reaction)	50	50	11

[a] Unless otherwise stated, reactions were performed in organic media. [b] HPA/H_2SO_4 (per proton). [c] In aqueous solution.

The relative activity of Keggin HPAs primarily depends on their acid strength. Other properties such as the oxidation potential, which determines the reducibility of HPA by reaction medium, as well as the thermal and hydrolytic stability are also important. These properties for the most common HPAs are summarized below:[4]

acid strength

$$\mathrm{PW} > \mathrm{SiW} \geq \mathrm{PMo} > \mathrm{SiMo}$$

oxidation potential

$$\mathrm{PMo} > \mathrm{SiMo} >> \mathrm{PW} > \mathrm{SiW}$$

thermal stability

$$\mathrm{PW} > \mathrm{SiW} > \mathrm{PMo} > \mathrm{SiMo}$$

hydrolytic stability

$$\mathrm{SiW} > \mathrm{PW} > \mathrm{SiMo} > \mathrm{PMo}$$

Usually, tungsten HPAs are the catalysts of choice because of their stronger acidity, higher thermal stability, and lower oxidation potential compared to molybdenum HPAs.[4] Generally, if the reaction rate is controlled by the catalyst acid strength, PW shows the highest catalytic activity in the Keggin series. However, in the case of less demanding reactions as well as in reactions at higher temperatures in the presence of water, SiW, having lower oxidation potential and higher hydrolytic stability, can be superior to PW.

The major problem, limiting the utility of homogeneously catalyzed processes, is the well-known difficulty in catalyst recovery and recycling. As the cost of HPAs is higher than mineral acids, the recycling of HPA catalysts is the key issue to their application. Only a few homogeneous reactions allow for easy HPA recycling, for example, hydration of olefins (see below). In some cases, HPA can be recovered from polar organic solution without neutralization by precipitating with a hydrocarbon solvent. HPA can also be extracted from an acidified aqueous solution of its salt with a polar organic solvent. Even though the neutralization of HPA is necessary, the amount of alkali needed and hence the amount of waste formed thereupon is much less than with mineral acids. A more efficient way to overcome the separation problem is the use of biphasic systems or solid HPA catalysts, which will be discussed later. Below are given selected examples of HPA-catalyzed homogeneous reactions. More can be found in refs 2−6, 8, 11, and 12.

1. Hydration of Olefins

The HPA-catalyzed hydration of C_3−C_4 olefins (eq 1) is an industrially important reaction, the hydration of propene being the first commercial process based on HPA catalysis.[10]

$$\mathrm{RCH{=}CH_2 + H_2O \rightarrow RCH(OH)CH_3} \qquad (1)$$

The hydration of isobutene is used for the separation of isobutene from the C_4 hydrocarbon stream produced by cracking. As the catalyst, a concentrated aqueous solution of HPA is used. Compared to mineral acids, such as H_2SO_4, HNO_3, and $HClO_4$, HPA is 2−4 times more active per equal H_3O^+ concentration and shows a higher selectivity, minimizing side reactions such as isobutene oligomerization.[113,114] Izumi et al.[11,113] showed that the reaction order with respect to HPA depends on the HPA concentration: first order in diluted HPA solution and nearly second order in concentrated solution. In contrast, the reaction with mineral acids is first order in the catalyst. The solubility of isobutene also significantly increases with increasing the HPA concentration. On these bases, a two-path reaction mechanism is suggested (Figure 8). 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 heteropolyanion with the carbenium ion driven by the soft basicity of heteropolyanion (see above). It is path II that is assumed to be responsible for promoting the reaction by stabilizing the intermediate carbenium ion in the above complex. From this mechanism the overall rate of the isobutene hydration, in agreement with experiment, can be expressed as

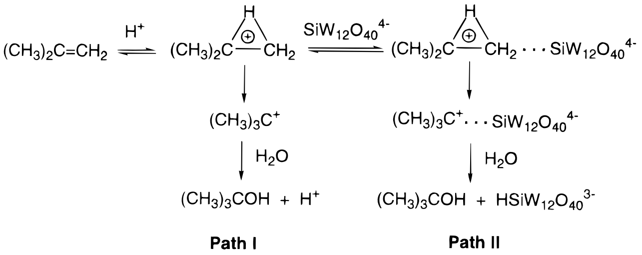


Figure 8. The mechanism of the hydration of isobutene.[113]

$$v = k_1[\mathrm{Ol}][\mathrm{H_3O^+}] + k_2[\mathrm{Ol}][\mathrm{H_3O^+}][\mathrm{HPA}^{n-}]$$

where k_1 and k_2 are the rate constants of paths I and II and [Ol] and $[\mathrm{HPA}^{n-}]$ are the concentrations of olefin and heteropolyanion, respectively.[113] On the other hand, as found later by Kozhevnikov et al.,[115] the rate of isobutene hydration catalyzed by HPAs obeys the Hammett plot: $\log k = -1.04H_o - 3.46$. And this plot is also valid for mineral acids such as H_2SO_4, HCl, HNO_3, and $HClO_4$. This may indicate that the reaction with both HPAs and mineral acids proceeds via the same principal mechanism, for example, path I. These authors[115] interpreted the high order with respect to HPA as a result of the strong specific salt effect of highly charged heteropolyanions. However, if considered on the molecular level, this explanation may be similar to what is suggested in path II by Izumi et al.[113]

HPAs were reported to be more efficient catalysts than H_2SO_4 and $HClO_4$ in the hydration of phenylacetylene[11] (eq 2).

$$\mathrm{PhC{\equiv}CH + H_2O \rightarrow PhCOCH_3} \qquad (2)$$

Cycloalkenes are hydrated to cycloalkanols with 99% selectivity in the presence of a catalyst consisting of a concentrated aqueous solution of an arylsulfonic acid and tungsten HPA.[116] PW and SiW are efficient catalysts for the homogeneous hydration of camphene to isoborneol, which is an intermediate in the synthesis of camphor.[117]

2. Esterification and Related Reactions

These reactions have been extensively studied in the presence of Keggin and Dawson HPAs as homogeneous catalysts.[4,11,112] Generally, such reactions are performed in organic media, and water greatly affects the reaction rate.[112] The catalytic activities of HPAs usually follow the order of their acid strengths,[4] as expected for Brönsted acid catalysis. However, Mo acids, having a higher oxidation potential than W ones, may exhibit a lower activity than expected from their acid strengths due to their reduction by the reaction medium.[4,11]

Recently Misono et al.[112] studied a series of homogeneous reactions such as decomposition of isobutyl propionate (IBP), transesterification of IBP with acetic acid and *n*-propyl alcohol, and esterification of propionic acid with isobutyl alcohol (eqs 3−6).

$$C_2H_5COOCH_2CH(CH_3)_2 \rightarrow (CH_3)_2C{=}CH_2 + C_2H_5COOH \quad (3)$$

$$C_2H_5COOCH_2CH(CH_3)_2 + CH_3COOH \rightarrow CH_3COOCH_2CH(CH_3)_2 + C_2H_5COOH \quad (4)$$

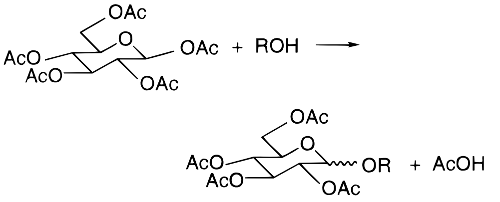
$$C_2H_5COOCH_2CH(CH_3)_2 + n\text{-}C_3H_7OH \rightarrow C_2H_5COOC_3H_7 + (CH_3)_2CHCH_2OH \quad (5)$$

$$(CH_3)_2CHCH_2OH + C_2H_5COOH \rightarrow C_2H_5COOCH_2CH(CH_3)_2 + H_2O \quad (6)$$

In reaction 3, HPAs are 60−100 times more active than H_2SO_4 and *p*-toluenesulfonic acid (TsOH). The activity is in the order PW > SiW ≥ GeW > BW > $H_6P_2W_{18}O_{62}$ > CoW. The same activity pattern was observed for reaction 4 in the absence of water. In contrast to reaction 3, the addition of water greatly accelerated reaction 4 and probably changed its course to proceed via the hydrolysis of IBP to propionic acid and isobutyl alcohol, followed by the esterification of isobutyl alcohol with acetic acid. On the other hand, for reactions 5 and 6 no significant difference in the activity between HPAs and H_2SO_4 was observed probably due to the leveling effect of the reactant alcohols on the acid strength of the catalysts.

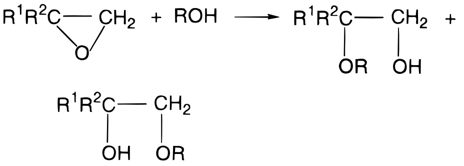
Dialkyl phthalates, utilized as plasticizers, were obtained by esterifying phthalic anhydride with C_8−C_{10} alcohols at 100−120 °C in the presence of PW (1−2%) as a homogeneous catalyst.[65] The catalytic activity of HPA is significantly higher than that of H_2SO_4 and TsOH. HPA supported on activated carbon can also be used as a heterogeneous catalyst. Although HPA/C is less active than the homogeneous PW catalyst, it can be easily separated from the reaction mixture and reused.

Synthesis of glycosides catalyzed by HPA is of industrial importance.[10] Glycosides are used as new effective and biodegradable surfactants. HPA is several times more active than the conventional catalysts such as TsOH and $ZnCl_2$. Thus acetylated monosaccharides interact readily with alcohols in a homogeneous phase in the presence of 2% of HPA with respect to the sugar derivative at 70−130 °C, yielding 70−90% of glycosides[118] (eq 7).



(7)

HPA is applicable as an active and selective catalyst in the homogeneous alcoholysis of epoxides (epichlorohydrin, 1,2-epoxybutane, isobutene oxide, styrene oxide, etc.) under rather mild conditions (45 °C, excess of alcohol)[11] (eq 8). HPA has much higher



(8)

activity than H_2SO_4 and TsOH. With H_2SO_4, in contrast to HPA, the rapid deactivation of the catalyst was observed probably due to the formation of an alkyl sulfate, resulting in loss of acidity. Likewise, in the acetolysis of epoxides, tetrahydrofuran, and linear esters, performed in an excess of acetic acid, HPA is far more effective than other acid catalysts such as TsOH and $BF_3{\cdot}H_2O$. And again, like with H_2SO_4, the activity of TsOH decreases in the early stage of the reaction due to the formation of a tosyl ester.[11]

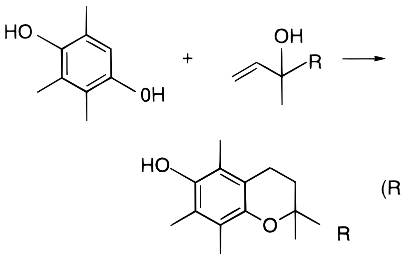
Methyl *tert*-butyl ether (MTBE)—a gasoline octane booster—is produced industrially on a large scale by reacting isobutene with methanol in the presence of an acid catalyst, e.g., acidic ion-exchange resin (eq 9). HPAs and their salts also catalyze the MTBE synthesis as homogeneous and heterogeneous catalysts.[2] Maksimov and Kozhevnikov[119] showed that in the homogeneous reaction at 42 °C, Keggin-type HPAs such as PW and SiW are 2−4 times more active than conventional catalysts in terms of the reaction rate per unit proton site. Interestingly, a Dawson-type HPA, $H_6P_2W_{18}O_{62}$, shows two times higher activity than the Keggin-type PW. However, with regard to the activity per unit weight of catalyst, H_2SO_4 is the most active catalyst. Recently liquid-phase synthesis of MTBE[120] and ethyl *tert*-butyl ether[121] by HPA-catalyzed etherification of *tert*-butyl alcohol with methanol and ethanol, respectively, has been studied.

$$(CH_3)_2C{=}CH_2 + CH_3OH \rightarrow CH_3OC(CH_3)_3 \quad (9)$$

3. Condensation

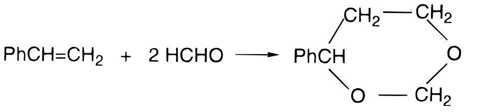
HPAs have long been known as catalysts for condensation reactions, e.g., the condensation of acetone to mesityl oxide and alkylbenzenes[4] and the condensation of ketones and phenols to bisphenols.[122]

Kozhevnikov et al.[123,124] have shown that HPA is an efficient catalyst for condensations in the syntheses of vitamins E, K_1 and C. Thus, PW and SiW catalyze the condensation of isophytol with 2,3,5-trimethylhydroquinone (TMHQ) to α-tocopherol (eq 10), which is the active form of vitamin E.[123] The reaction is performed in a homogeneous phase (e.g., in butyl acetate or acetic acid) or in a heterogeneous system (e.g., in toluene) with ~1 wt % HPA based on TMHQ. With HPA, practically the same yield and quality of vitamin E is obtained as with $ZnCl_2$ which is the best commercial catalyst. However, $ZnCl_2$ is used in a stoichiometric amount, resulting in a large amount of waste. In contrast to $ZnCl_2$, HPA can be recovered after the reaction and reused.



(R=C_{16} alkyl) (10)

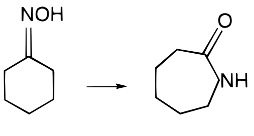
HPA catalyzes the Prins reaction of alkenes with formaldehyde to yield 1,3-dioxanes. Thus in the reaction of styrene (eq 11), Keggin-type HPAs were shown to be superior to H_2SO_4 and TsOH, the activity differing only slightly in the series of HPAs.[11]



(11)

4. Miscellaneous Reactions

Izumi and Fujita[125] reported that an iminium salt, prepared by interacting *N*,*N*-dimethylformamide with epichlorohydrin in the presence of PW or SiW, effectively catalyzes the liquid-phase Beckmann rearrangement of cyclohexanone oxime to ϵ-caprolactam (eq 12) under mild conditions (50−60 °C). The product lactam was found to poison the catalyst, although reversibly. The turnover of the catalyst attained 200.



(12)

HPAs have long been known as very efficient catalysts for the decomposition of cumene hydroperoxide to phenol and acetone[126,127] (eq 13). Similarly,

$$PhC(CH_3)_2OOH \rightarrow PhOH + CH_3COCH_3 \qquad (13)$$

1,3,5-trihydroxybenzene is formed via the decomposition of 1,3,5-triisopropylbenzene hydroperoxide at 50−100 °C with 97% selectivity at 89% hydroperoxide conversion.[128]

1,2-Diols (1,2-propanediol, 2,3-butanediol, and 2,3-dimethyl-2,3-butanediol) readily undergo the pinacol rearrangement to yield the corresponding carbonyl compounds (propanal, 2-butanone, and 3,3-dimethyl-2-butanone, respectively) in the presence of PW, SiW, PMo, and SiMo. 1,4- and 1,5-diols under such conditions selectively form cyclic ethers.[129]

Kortz and Pope[130] have synthesized and fully characterized two new polyoxomolybdate diphosphate complexes with the formula $[(O_3PXPO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ (X = O or CH_2). The polyanion with X = O is a possible intermediate in the molybdate-catalyzed hydrolysis of pyrophosphate at pH 2.

C. Biphasic Reactions

Separation of products and recovery and recycling of a catalyst often becomes much easier if a homogeneously catalyzed reaction can be performed in a biphasic system consisting of two immiscible liquid phases—a catalyst phase and a product/reactant phase—with intense mass transfer between them. HPAs due to their special solubility properties, i.e., high solubility in a variety of polar solvents and insolubility in nonpolar solvents, are suitable catalysts for operating under phase-transfer conditions. There are two types of such biphasic systems: (1) initially homogeneous, a reaction system separates in two liquid phases in the course of the reaction; and (2) a reaction system is biphasic from the very beginning. The catalyst phase, usually the lower one, is a solution of HPA in a polar reactant. The reaction predominantly proceeds in the catalyst phase, and the product formed is transferred to the less polar product phase. The amount of HPA in the product phase must be negligible to allow easy catalyst separation.

1. Polymerization of Tetrahydrofuran

Polymerization of tetrahydrofuran (THF) is used for the preparation of polyoxytetramethylene glycol (PTMG), which is employed for manufacturing Spandex fibers and polyurethanes. PTMG is commercially produced by a two-step process, including ring-opening polymerization of THF with acetic anhydride catalyzed by $HClO_4$, followed by hydrolysis of the terminal acetate groups in the prepolymer. Izumi et al.[131] found that HPA is more active than $HClO_4$ in the polymerization of THF. Aoshima et al.[132] have developed a one-step process for the THF polymerization to directly yield PTMG (eq 14).

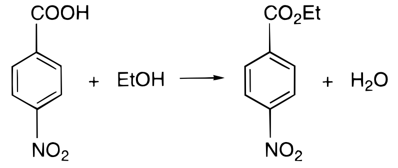
$$n\mathrm{THF} + H_2O \rightarrow HO[(CH_2)_4O]_nH \qquad (14)$$

PTMG is obtained by ring opening THF with water in the presence of PW at 60 °C. The H_2O/PW molar ratio is critical for the process, controlling the reaction rate and molecular weight of polymer. When the H_2O/PW molar ratio is above 15, a homogeneous phase forms, and no reaction takes place. When the H_2O/PW ratio is below 15, the solution separates in two liquid phases—a THF (upper) phase and a PW−THF−H_2O (lower) phase. The polymerization starts when H_2O/PW ratio is decreased below 10. The polymer is formed in the HPA phase and transferred to the THF phase. The reaction rate increases with decreasing H_2O/PW ratio, and so does the molecular weight of polymer. The process is performed continuously. The PTMG with a molecular weight of 500–2000 and a narrow molecular weight distribution is obtained from the THF phase.

Similarly, PW and PMo catalyze the polymerization of cyclic formaldehyde acetal and trimer, 1,3-dioxolane and 1,3,5-trioxane, respectively. Thus, in the polymerization of 1,3,5-trioxane, the comparable reaction rates can be obtained with 25 times less a catalyst consumption on weight basis than for conventional catalyst like $BF_3{\cdot}OR_2$.[133]

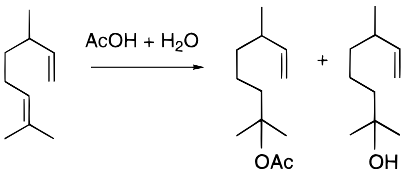
2. Esterification

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 (eq 15) in the presence of PW (3–7 wt %) at 75 °C.[5] Water formed in the reaction course is separated by azeotropic distillation 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. The catalyst phase is easily separated and can be reused.



(15)

Acetoxylation and hydration of dihydromyrcene (DHM) yield dihydromyrcenol (DHM-OH) and dihydromyrcenyl acetate (DHM-OAc) (eq 16), respectively, which are useful as perfume ingredients.

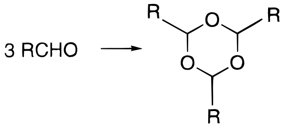


(16)

These reactions occur simultaneously in a two-phase system in the presence of HPA at 14–30 °C.[134] The upper phase mainly consists of DHM and the lower phase is a concentrated solution of PW in aqueous acetic acid. Acetic acid is approximately equally distributed between the two phases. The reaction proceeds in the catalyst phase to form DHM-OH and DHM-OAc, which are transferred to the DHM phase. The process reaches an equilibrium at ~30% DHM conversion and is strongly complicated by acid-catalyzed isomerization and cyclization of DHM. This method provides 90% selectivity to the sum of DHM-OH and DHM-OAc at 21% DHM conversion. The catalyst phase can be reused without loss of activity.

3. Other Reactions

Keggin-type HPAs such as PMo, PW, and SiW catalyze the cyclotrimerization of aldehydes, such as ethanal, propanal, butanal, 2-methylpropanal, etc., to produce 2,4,6,-trialkyl-1,3,5-trioxanes in high yields (eq 17), as reported by Sato et al.[135,136] Catalyst turnover number is more than 10 000 for the propanal cyclotrimerization. At high conversions of aldehyde, the reaction mixture spontaneously separates into two phases, a product phase and a catalyst phase, which, depending on aldehyde can be solid or liquid. For the propanal cyclotrimerization, the reaction mixture separates into two liquid phases, and the recovered catalyst phase can be easily reused. Vapor-phase trimerization of formaldehyde to trioxane catalyzed by $H_4PMo_{11}VO_{40}$ supported on silicon carbide at 110 °C has been studied.[137]



(17)

Sato et al.[138] examined various acetal formation reactions between monoalcohols or diols and a range of aldehydes or ketones catalyzed by a Keggin-type HPA in comparison with other acid catalysts. The reaction was strongly inhibited by water produced in the reaction course. The catalyst activity was found to decrease in the order: SiW > PMo > PW > TsOH > H_2SO_4. For several reactions between a carbonyl compound and a diol, the reaction mixture was spontaneously separated into two liquid phases, enabling easy catalyst recycling.

Timofeeva and Kozhevnikov[139] reported the alkylation of hydroquinone with isobutene to yield 2-*tert*-butylhydroquinone and 2,5-di-*tert*-butylhydroquinone catalyzed by $H_3PW_{12}O_{40}$, $H_6P_2W_{18}O_{62}$, and $H_6P_2W_{21}O_{71}$ under phase-transfer conditions in a biphasic system, including toluene (upper phase) and HPA dioxane etherate, HPA–$xC_4H_8O_2$–yH_2O (lower phase). In this case, the two phases are immiscible from the very beginning, and the products are obtained from the toluene phase. The yield of 2-*tert*-butylhydroquinone increases in the series: $H_6P_2W_{18}O_{62} < H_6P_2W_{21}O_{71} < H_3PW_{12}O_{40}$, with $H_3PW_{12}O_{40}$ being 70% (85 °C). $H_3PW_{12}O_{40}$ showed a higher efficiency than H_2SO_4 or H_3PO_4.

D. Heterogeneously Catalyzed Liquid-Phase Reactions

In this section, reactions in liquid–solid systems catalyzed by bulk and supported HPAs and their insoluble salts are discussed. In heterogeneous as well as in homogeneous systems, HPAs are generally more efficient than conventional catalysts, such as SiO_2-Al_2O_3, zeolites, etc., which is in line with their relative acid strengths.[2,4,8,11] Obvious advantage of heterogeneous systems over homogeneous is easy separation of a catalyst from reaction products. Furthermore, since HPAs are soluble only in wet nucleophilic solvents, levelling the acid strength (dehydrated HPAs are scarcely soluble in dry polar media), their intrinsic strong acidity cannot be fully utilized in homogeneous systems. Hence, for catalyzing highly demanding reactions, e.g., the Friedel–Crafts reaction, HPA must be used as a solid acid catalyst in a dry nonnucleophilic medium. To enhance the acid strength, solid HPA catalysts are usually dehydrated by evacuating at 150−300 °C for 1−2 h.[4]

A serious problem with the solid HPA catalysts is their deactivation during organic reactions due to the formation of carbonaceous deposit (coke) on the catalyst surface. This problem remains to be solved to put heterogeneous HPA catalysis in practice. Conventional regeneration by burning coke at 500−550 °C, which is routinely used in the case of aluminosilicates and zeolites, is not applicable to HPAs because their thermal stability is not high enough to do so. Supporting HPA on a carrier inhibits the formation of coke,[11] while bulk HPAs, having very strong acid sites and low surface area, coke more rapidly.

1. Paraffin Alkylation

The paraffin alkylation is utilized in industry for obtaining higher octane paraffins which are blended into gasoline. H_2SO_4 or HF are used as homogeneous catalysts in this process. PW supported (75%) on a series of carriers, such as mesoporous molecular sieve MCM-41, amorphous silica, and alumina, has been studied as the catalyst for the isobutane/2-butene alkylation in comparison with a MCM-22 zeolite.[76] The reaction was performed in a stirred autoclave at 120 °C and 30 atm with a 50:1 isobutane/2-butene feed. The greatest olefin conversion (87%) was observed with PW/MCM-41. The alkylate quality (trimethylpentane to dimethylhexane ratio) observed with PW/MCM-41, albeit worse compared with MCM-22, is better than with PW/SiO_2 or PW/Al_2O_3.

2. Friedel−Crafts and Related Reactions

HPAs and their salts are promising solid acid catalysts for Friedel−Crafts reactions, to replace the conventional homogeneous catalysts such as $AlCl_3$, BF_3, and H_2SO_4, which bring about serious environmental and operational problems—high toxicity, corrosion, spent acid disposal, difficulty of separation and recovery, etc.[11]

Izumi et al.[11] found that silica-supported PW is a very active catalyst, superior to other HPAs, for the alkylation of benzene with 1-octene. At a low reaction temperature of 35 °C and an excess of benzene, the major product is 2-phenyloctane (50−80 mol %), 3- and 4-phenyloctanes also being formed. The catalytic activity depends on the pretreatment temperature and the HPA loading. In contrast, in the alkylation of arenes with benzyl chloride, the most efficient catalyst is PMo/SiO_2.

In the acylation of *p*-xylene with benzoyl chloride, however, PMo in the PMo/SiO_2 catalyst was found to decompose during the reaction.[11] Probably, the real active species is not the supported PMo, but some soluble species which might be formed by the interaction between PMo and benzoyl chloride. In contrast to PMo, SiW and PW both effectively catalyze the acylation and remain unchanged on the SiO_2 surface after the reaction. But in a more polar reaction medium, as in the acylation of chlorobenzene, even SiW leaches from the silica support and decomposes in the course of the reaction like PMo. Benzoic anhydride can be used as an acylating agent with the SiW/SiO_2 catalyst, but benzoic acid cannot. A weaker solid acid, SiW/carbon, can also catalyze the acylation, but less efficiently than SiW/SiO_2.[11]

Table 5. Friedel−Crafts Acylation[142]

substrates		product yield[a]	
acylating agent	arene	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	$H_3PW_{12}O_{40}$
$(PhCO)_2O$	*p*-xylene	57	3
$(PhCO)_2O$	anisole	85	69
Ac_2O	anisole	89	50
n-$C_7H_{15}COCl$	mesitylene	80	44

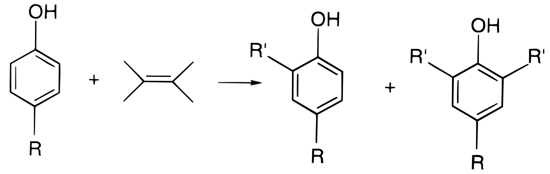
[a] Acylating agent/arene/catalyst = 5/100/0.01 mmol, reflux, 2 h.

As found by Soeda et al.,[140] bulk PW shows a better performance than liquid (H_2SO_4, CF_3COOH) or solid (Amberlyst-15, SiO_2-Al_2O_3) catalysts for the selective alkylation of *p*-xylene with isobutene at 30 °C to afford *tert*-butyl-*p*-xylene—an important precursor for liquid crystalline polymers—with 75% selectivity.

Misono, Okuhara, et al.[53,54,141] demonstrated that the insoluble salt $Cs_{2.5}H_{0.5}PW$, which has a large surface area and strong acid sites, is a promising solid acid catalyst for Friedel−Crafts reactions. In the alkylation of 1,3,5-trimethylbenzene by cyclohexene, this salt was found to be more active than the parent acid PW.[53] It was suggested that the higher hydrophobicity of the Cs salt compared to HPA is beneficial for the adsorption of the nonpolar reacting molecules. In addition, it was claimed that the Cs^+ cation could favorably change the softness of heteropolyanion, thus enhancing the stabilization of the intermediate cyclohexyl cation by the polyanion.

$Cs_{2.5}H_{0.5}PW$ shows high efficiency in acylation of activated arenes, such as p-xylene, anisole, mesitylene, etc., by acetic and benzoic anhydrides and acyl chlorides (Table 5). This catalyst provides higher yields of acylated arenes than the parent PW, the latter being partly soluble in the reaction mixture.[142]

Bulk and silica-supported tungsten HPAs are very efficient and versatile catalysts for alkylation, dealkylation, and transalkylation of phenols[143−149] (eqs 18−20). Such reactions are widely used for the preparation of antioxidants, bioactive substances as well as for positional protection in organic synthesis. As found by Kulikov et al.,[143−146] PW is much more active



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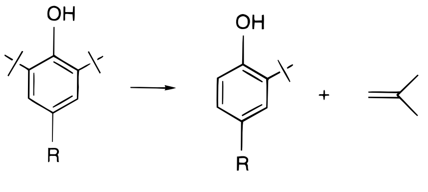

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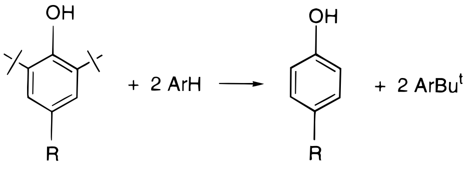

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Table 6. Alkylation of *p-tert*-Butylphenol (TBP) by Styrene Catalyzed by PW/MCM-41[a,76]

catalyst	selectivity, mol % I	II	other products
PW	23	68	9
40% PW/MCM-41	66	21	13
40% PW/SiO_2	24	64	12

[a] 4.0 wt % catalyst, in *n*-octane, 105 °C, 90% TBP conversion.

than conventional catalysts, such as H_2SO_4, ion-exchange resin, aluminosilicates, etc., generally providing higher yields of products. Even Nafion-H, a perfluorinated ion-exchange resin comparable in its acid strength to 100% H_2SO_4, is less active than PW.[146]

The *trans*-de-*tert*-butylation of phenols (eq 20, where ArH = *o*-xylene) is first order with respect to both phenol and HPA.[147] With PW/SiO_2 catalysts, the rate depends dramatically on HPA loading. The rate based on the HPA weight increases with increasing HPA loading, passing a maximum at 30 wt % HPA loading. 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. In contrast, the rate based on the amount of surface protons, increases monotonously with HPA loading as the acid strength increases.

The alkylation of *p*-cresol with isobutene (eq 18, where R = CH_3 and R′ = $C(CH_3)_3$) with the use of PW instead of H_2SO_4 has been commercialized in Russia.[5] It is a step in the synthesis of antioxidants. The use of HPA provides the gain in selectivity of 7−10% and almost completely eliminates toxic water pollution in the process.

Phenols can be alkylated with a terminally unsaturated olefin polymer in the presence of HPA. Thus ethylene/1-butene copolymer (M_n 3300) was used to alkylate phenol in *o*-dichlorobenzene with PW precalcined at 300 °C as the catalyst. The alkylphenols so formed are useful as precursors for the preparation of fuel and lubricant additives.[149]

PW supported (20−50 wt %) on a mesoporous pure-silica molecular sieve MCM-41, having 30 Å uniformly sized pores, exhibits a higher catalytic activity than H_2SO_4 or bulk PW and shows shape selectivity in alkylation of 4-*tert*-butylphenol with olefins[75] (eq 18, where R = $C(CH_3)_3$). In the alkylation with styrene, PW/MCM-41 provides a higher yield of the monosubstituted product 2-(1-phenylethyl)-4-*tert*-butylphenol (I) than bulk PW or PW supported on amorphous silica, at the expense of the more bulky disubstituted product 2,6-bis(1-phenylethyl)-4-*tert*-butylphenol (II) (Table 6). HPA/MCM-41 may be a promising solid acid catalyst for conversion and formation of organic compounds of large molecular size.

3. Esterification, Hydrolysis, and Related Reactions

There is a strong demand for new solid acid catalysts, having advanced characteristics, to replace conventional liquid and solid catalysts, such as sulfuric acid and ion-exchange resins, in the title reactions.[11] Sulfuric acid, as already mentioned, poses serious environmental and operational problems. Acidic ion-exchange resins such as Amberlyst-15 are widely employed, but only at temperatures below 100 °C due to their low thermal stability. It should be noted that in these reactions in which water participates as a reactant or a product, there are only a few solid acid catalysts that may meet the criteria of activity and stability. As demonstrated by Izumi et al.,[11,103] certain supported HPA catalysts as well as insoluble HPA salts have advantages as catalysts for liquid-phase reactions in aqueous media because they are practically insoluble, thermally more stable than acidic resins and have strong acidity.

Active carbon strongly adsorbs a certain amount of HPA, and carbon-supported HPAs thus obtained catalyze liquid-phase esterification and related reactions in polar media.[11] The maximum HPA loading tightly retained on carbon in water or methanol is ∼10 wt %, slightly depending on the type of carbon and its pretreatment. The carbon-supported PW catalyze the formation of butyl *tert*-butyl ether from *n*-butyl alcohol and *tert*-butyl alcohol at 106 °C and the esterification of acetic acid with *n*-butyl alcohol at 60 °C.[11] Schwegler et al.[65] applied this catalyst for the esterification of phthalic anhydride with C_8−C_{10} alcohols at 100−120 °C to yield dialkyl phthalates. In all these reactions, the catalyst can be reused, no HPA leaching from carbon being observed. However, the carbon-supported HPA catalysts have a rather low catalytic activity because of their weak acidity. In addition, active carbon strongly adsorbs polar organic substances which makes the work-up procedure more difficult.

Dupont and Lefebvre[150] have studied the esterification of propanoic acid by butanol or 2-ethylhexanol catalyzed by SiW and PW pure or supported on carbon supports. In the homogeneous reaction the reaction rate was proportional to the concentration of protons. Accordingly, SiW showed slightly higher activity than PW. Carbon-supported HPAs in all cases exhibited lower activity than the pure HPAs, the activity depending on the carbon support and the HPA loading. In addition, a deactivation occurred during the recycling of these catalysts due to the leaching of HPA from support.

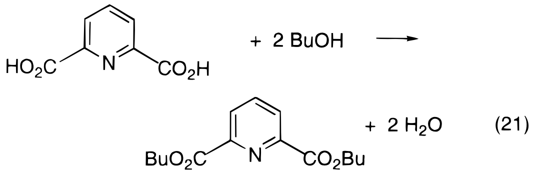
Izumi et al.[102] showed that the insoluble salt $Cs_{2.5}H_{0.5}$PW is an active solid acid catalyst for esterification and hydrolysis. For example, it is much more active than zeolite H-ZSM-5 for the hydrolysis of ethyl acetate and esterification of acetic acid with ethanol.[102] However, $Cs_{2.5}H_{0.5}$PW, consisting of very fine particles (∼10 nm), readily forms a colloidal solution in water or alcohol, which makes it inseparable by filtration.

As reported recently,[103] $Cs_{2.5}H_{0.5}$PW and even PW itself, which is highly soluble in water, can be included in the silica matrix by means of a sol−gel technique to be water insoluble and easily separable microporous solid acid catalysts. The catalysts thus obtained have large surface areas (400−800 m^2 g^{-1}), strong acidity and are thermally more stable than Amberlyst-15. They effectively catalyze the hydrolysis of ethyl acetate in aqueous phase, showing higher turnover rates than Amberlyst-15 and H-ZSM-5. Remarkably, the immobilization of PW into the silica matrix effectively suppresses the HPA leaching to as low as 0.3% during the hydrolysis reaction (60 °C, 3 h). Note that in the case of the usual silica-supported PW catalyst, HPA completely dissolves in the reaction medium. Interestingly, the catalytic activity of the silica-included HPA is higher than the homogeneous acid. It is suggested that PW is entrapped in the silica network as a highly concentrated aqueous solution, and the silica network is probably narrow enough to prevent the Keggin anion from leaching outside. It is expected that silica-included heteropoly compounds may find wide applications to acid-catalyzed liquid-phase reactions in aqueous media as potential alternatives for H_2SO_4 and ion-exchange resins.[103]

In the acetoxylation of dihydromyrcene (DHM) (eq 16), the 40% PW/SiO_2 catalyst shows a comparable activity with the homogeneous PW catalyst, while the selectivity of the solid catalyst is higher.[134] The latter is probably because it is more difficult for a carbenium ion intermediate to isomerize on the catalyst surface than in solution. With a stoichiometric 1:1 DHM−AcOH mixture, no PW leaching from the catalyst was observed. The PW/SiO_2 catalyst can be reused; however, a gradual deactivation was observed. Bulk PW had a very low activity, if any, probably due to the small surface area and the blocking of proton sites by DHM oligomers.

Okuhara et al.[141] reported that $Cs_{2.5}H_{0.5}$PW is more active for liquid-phase cyclohexyl acetate decomposition than such solid acid catalysts as Nafion-H, HY, and H-ZSM-5 zeolites, and SO_4^{2-}/ZrO_2.

Timofeeva et al.[151] found that the esterification of dipicolinic acid (DA) with butanol (eq 21), which is a step of the synthesis of pharmaceutics, is catalyzed by PW as well as by its insoluble salts. 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^{3+} salt, $Ce_{0.87}H_{0.4}$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, $Ce_{0.87}H_{0.4}$PW can be easily separated and reused. Insoluble NH_4^+, K^+, and Cs^+ salts of PW showed only moderate activities in this reaction.



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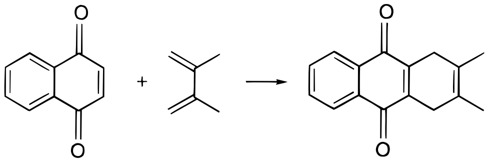
4. Miscellaneous Reactions

Silica-supported PW has been found to be an active and recyclable catalyst for the Diels−Alder reaction (eq 22) in toluene medium, providing a 70−80% yield.[152] The Ce^{3+} salt, $Ce_{0.87}H_{0.4}$PW, showed a fairly high activity too, while $Cs_{2.5}H_{0.5}$PW was practically inactive. Bulk PW exhibited a very low activity probably due to the small surface area and site blocking by diene polymers.



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III. Multicomponent Polyoxometalates in Liquid-Phase Oxidation

The liquid-phase oxidation of organic substances catalyzed by polyoxometalates (POM) proceeds in homogeneous or biphasic systems, dioxygen, hydrogen peroxide, alkylperoxides, etc., being applied as oxidants. In contrast to acid catalysis, where easily available classical Keggin-type HPAs dominate, in the liquid-phase oxidation, a wide variety of transition metal-substituted heteropolyanions are used. Multicomponent POM redox catalysts are considered as robust oxidation-resistant inorganic metalloporphyrin analogs.[12,16,153] The state of POMs in solution is generally complicated by a series of pH-dependent equilibria, involving a variety of polyanions and mononuclear metallospecies. These equilibria, with a few exceptions, are largely unknown. As a result, relatively little exact knowledge of mechanisms of POM-catalyzed oxidation is available. In this part, we will discuss oxidations with the use of the most important and environmentally benign oxidants—dioxygen and hydrogen peroxide. Several reviews on catalysis by POM in the liquid-phase oxidation have been published.[2,3,6,12,13,16,154,155]

A. Oxidation with Dioxygen

This section mainly reviews recent applications of Keggin-type mixed-addenda heteropolyanions $PMo_{12-n}V_nO_{40}^{(3+n)-}$ (HPA-*n*) as catalysts for aerobic liquid-phase oxidation. Here HPA-*n* can mean either anion or acid as well as a partially protonated anion. The HPA-*n* catalytic system, discovered by Matveev et al.[1,156] in the 1970s, is the most efficient and versatile one in the POM series for oxidation by O_2.[3,157−159] Discussed are HPA-*n*-catalyzed reactions in homogeneous, biphasic, and heterogeneous systems as well as mechanistic aspects of the HPA-*n* catalysis. It should be noted that a HPA-*n*-based catalyst is used in industry for the gas-phase oxidation of methacrolein to methacrylic acid.[10] Numerous attempts have been made to perform aerobic oxidations by other kinds of POM; for a review, see ref 16.

1. General Principles

In liquid-phase oxidation, HPA-*n* with $n = 2-6$ are used. These compounds are remarkable because they are the reversibly acting oxidants under mild conditions.[1,3] The presence of a certain number of V ions in the heteropolyanions is essential. Thus, the all-molybdenum anion $PMo_{12}O_{40}^{3-}$ (HPA-0) fails to possess such redox properties under mild conditions; so does HPA-1 for reasons that will be discussed later.

Generally reactions catalyzed by HPA-*n* proceed via a stepwise redox mechanism represented by eqs 23 and 24:

$$\text{HPA-}n + \text{Red} + m\text{H}^+ \rightarrow \text{H}_m(\text{HPA}-n) + \text{Ox} \quad (23)$$

$$\text{H}_m(\text{HPA-}n) + (m/4)\text{O}_2 \rightarrow \text{HPA-}n + (m/2)\text{H}_2\text{O} \quad (24)$$

This mechanism includes stoichiometric *m*-electron oxidation of the substrate, Red, by HPA-*n* to form the product, Ox, followed by reoxidation of the reduced form of the oxidant, H_m(HPA-*n*), with dioxygen, where $H_m(\text{HPA-}n) = H_m(PMo_{12-n}{}^{6+}V_{n-m}{}^{5+}V_m{}^{4+})^{(3+n)-}$. Actually, it is the $V^{5+} \leftrightarrow V^{4+}$ transformation that is responsible for the redox properties of HPA-*n*. The reduction of HPA-*n* in solution is accompanied by protonation to maintain the charge of the polyanion.[19] In aqueous solution, HPA-*n* are generally used in the pH range from 0.5 to 3.5, where they are relatively stable.

Operationally, reactions 23 and 24 can be carried out in the same reactor (one-stage process) or separately as a combination of two stoichiometric reactions (two-stage process).[1,3] Thus HPA-*n* combines the advantages of stoichiometric and catalytic oxidations.

As the catalysts, either one-component or two- and multicomponent systems are used. The most important two-component system includes HPA-*n* and Pd(II). Other two-component systems are also known, e.g., those including complexes of Pt, Ir, Ru, etc.[3,6]

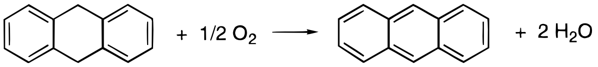
The thermodynamic condition for the occurrence of reactions 23 and 24 can be represented using redox potentials of the substrate, HPA-*n*, and dioxygen: $E(\text{Red}) \leq E(\text{HPA-}n) \leq E(O_2) = 1.23$ V.[3] The redox potential E(HPA-*n*) is 0.7 V vs normal hydrogen electrode (NHE) for HPA-*n* with $n = 1-4$ at pH 1.[160] Hence the above condition fulfills for a wide variety of organic substrates as well as for many inorganic redox systems to be used as cocatalysts with HPA-*n*. Some other POM having similar properties, e.g., $PMo_6W_6{}^{3-}$, can also be used for this purpose.[11]

2. Homogeneous Oxidation

One-Component HPA-*n* System. A range of hydrocarbons can be homogeneously oxidized with HPA-*n* as a catalyst under mild conditions. HPA-*n* catalyzes the oxidation of alkanes to oxygenates by O_2. Arzamaskova et al.[161] and Geletii and Shilov[162] reported the oxidation of alkanes by HPA-6 under mild conditions in the presence Ru(III), Ir(III),[161] and Pt(II).[162] More recently Lyons et al.[163] have oxidized alkanes by O_2 with HPA-*n* as one-component catalyst. For example, propane is oxidized in an AcOH-H_2O solution in the presence of HPA-*n* at 150 °C to give a mixture of isopropyl alcohol and acetone in 42% and 52% selectivity, respectively[163] (eq 25). The mixed-addenda HPA-*n* are more efficient catalysts than the all-molybdenum heteropolyanions. Other types of POM are also active, e.g., a trisubstituted Keggin anion $PW_9Fe_2NiO_{37}{}^{7-}$.[164] As shown by Mizuno et al.,[165] this polyanion also catalyzes the oxidation of cyclohexane, adamantane, cyclohexene, and ethylbenzene. Neumann et al.[166] reported that a new Ru^{3+}-substituted POM, $(WZnRu_2)(OH)(H_2O)(ZnW_9O_{34})_2{}^{11-}$, catalyzes the hydroxylation of alkanes by O_2.

$$C_3H_8 + O_2 \rightarrow CH_3CH(OH)CH_3 + CH_3COCH_3 \quad (25)$$

Many synthetically attractive oxidations of hydrocarbons have been developed to date. For example, highly efficient dehydrogenations with HPA-2 in CH_2ClCH_2Cl/tetraglyme solution have been reported by Neumann et al.[167] Thus reaction 26 yields 98% anthracene (70 °C, 16 h).



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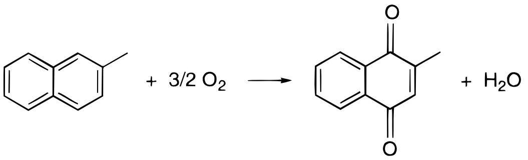
The HPA-2-catalyzed dehydrogenation of α-terpinene to *p*-cymene in acetonitrile solution was found to be zero order in α-terpinene, first order in dioxygen, and second order in HPA-2.[158,168] On the basis of these kinetic results and spectroscopic data, a reaction scheme was formulated. The scheme involves the formation of a stable substrate–catalyst complex in the catalyst reduction stage (eq 23) and a *μ*-peroxo catalyst intermediate in the catalyst reoxidation stage (eq 24) where dioxygen is reduced in a four-electron redox reaction. However the above kinetic evidence may not be sufficient to support the *μ*-peroxo catalyst intermediate.

Oxidation of 2-methylnaphthalene to quinone (eq 27) is a step of the vitamin K_3 synthesis. In industry it is carried out with highly toxic CrO_3 as a stoichiometric oxidant with a low yield (~50%). With HPA-*n*, we have succeeded to carry out the catalytic oxidation in AcOH-H_2O solution at 120–140 °C with 82% selectivity at 78% conversion.[169]



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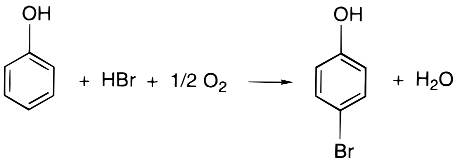
Gorodetskaya et al.[170] reported oxidative bromination of a range of aromatics catalyzed by HPA-*n* with HBr as a brominating agent and O_2 as a terminal oxidant. More recently Neumann et al.[171] reported the oxidative bromination of phenols in the *para* position (eq 28) in a homogeneous HPA-2–CH_2ClCH_2Cl–tetraglyme system with a remarkably high 99% yield (20 °C, 5 h).



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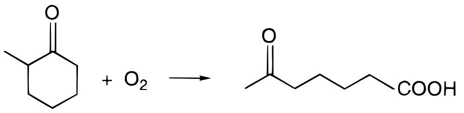
Ishii et al.[172] have studied a number of oxidations with O_2 in the presence of an aldehyde, e.g., 2-methylpropanal, as a sacrificial reductant and $(NH_4)_5H_4PMo_6V_6O_{40}$ as a catalyst in dichloroethane solution. (The addition of aldehydes is a well-known method to promote the liquid-phase free-radical oxidation of organic compounds by O_2; many metal complexes, e.g., Co^{3+}, Mn^{3+}, Cu^{2+}, Fe^{3+}, etc., can initiate such reactions.[173]) Thus the epoxidation of olefins proceeds at 25 °C with a very high selectivity of 81–100% (eq 29).

$$\text{alkene} + O_2\ (+\ \text{RCHO}) \rightarrow \text{epoxide}\ (+\ \text{RCOOH}) \quad (29)$$

A carboxylic acid as a cooxidation product is also formed. In addition, the Baeyer–Villiger oxidation of cyclic ketones to lactones was accomplished with 78–87% selectivity by using benzaldehyde as the sacrificial aldehyde (25 °C, 20 h, 1 atm O_2). These reactions may be synthetically useful if the carboxylic acid is a useful product, provided a less harmful solvent instead of CH_2ClCH_2Cl is employed.

Mizuno et al.[174] reported that the selective epoxidation of olefins by O_2 in the presence of an aldehyde is also catalyzed at 25 °C by transition metal-substituted 12-tungstophosphates, $PW_{11}O_{39}M^{x-}$, where M = Co, Mn, Fe, Cu, or Ni, whose activity decreases in that order. The order of the effectiveness of the aldehydes is: pivalaldehyde > isobutyraldehyde >> butyraldehyde ≥ acetaldehyde > valeraldehyde > benzaldehyde. The catalytic activity of POMs is solvent dependent. Thus the activity of $PW_{11}Co$ decreases in the series: $CHCl_3 > CH_2Cl_2 > 1,2\text{-}C_2H_4Cl_2 \geq CH_3CN > C_6H_6 >$ DMF > DMSO. POM-catalyzed co-oxidative epoxidation of olefins with O_2 in the presence of aldehyde apparently proceeds by a radical-chain mechanism.[172,175,176]

A variety of oxygenates, e.g., aldehydes, ketones, phenols, etc., can be oxidized with HPA-*n* under mild conditions with very good yields. Brégeault et al.[177] reported the oxidative cleavage of cyclic ketones. For example, the cleavage of 2-methylcyclohexanone is catalyzed by HPA-4 in aqueous solution to yield 97% of ketoacid (60 °C, 8 h) (eq 30). HPA-*n*-catalyzed oxidation of cyclohexanone to adipic acid was studied as an alternative to the industrial nitric acid oxidation.[177] The reaction was found to be solvent dependent, aqueous acetic acid being the best solvent, yielding 50% adipic acid together with 19% glutaric and 3% succinic acids at 99% cyclohexanone conversion (HPA-4, 1 atm O_2, 70 °C, 7 h). Moreover, adipic acid was stable to degradation by HPA-*n*/O_2 system. The advantage of this system, compared to the nitric acid oxidation, is less corrosion and no nitric oxides evolved. However the selectivity to adipic acid is still not high enough.



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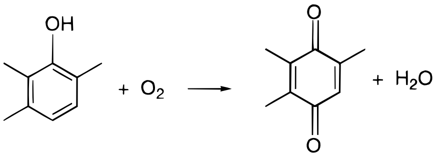
Ishii et al.[172] studied the oxidation of aldehydes to carboxylic acids with the use of the NH_4^+ salt of HPA-6 as a catalyst (eq 31). The reaction proceeds under very mild conditions (25 °C, 1 h) in dichloroethane with 96–100% selectivity at 60–78% aldehyde conversion.

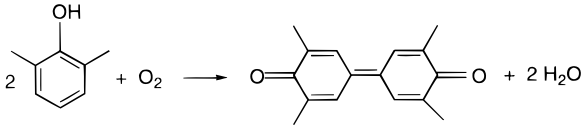
$$\text{RCHO} + {}^{1}\!/_{2}O_2 \rightarrow \text{RCOOH} \qquad (31)$$

Neumann et al.[178] and ourselves[179,180] reported oxidations of alkylphenols. The oxidation of 2,3,5-trimethylphenol (TMP) to trimethylbenzoquinone (TMBQ) (eq 32) is of practical interest as a step to synthesize vitamin E. This reaction yields TMBQ with 86% selectivity at 100% TMP conversion (HPA-4, AcOH-H_2O, 50 °C).[179]



(32)

The oxidative coupling of 2,6-dialkylphenols to diphenoquinones (eq 33) catalyzed by copper amine complexes is used for the synthesis of antioxidants.



(33)

In this reaction, HPA-*n* shows a higher activity than copper complexes. The oxidative coupling proceeds in H_2O, AcOH-H_2O, or MeOH-H_2O as solvents at 25–50 °C under 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-*tert*-butyldiphenoquinones have been obtained in a nearly 100% yield. The catalyst can be recycled without loss of its activity.[179]

Oxidation of sulfur compounds can be efficiently carried out with HPA-*n*. For example, the oxidation of H_2S to sulfur[181] and thioethers to sulfoxides and sulfones[182] proceeds with nearly 100% yield. Harrup and Hill[183] have reported POM-based catalytic systems—$ZnPW_{11}O_{39}{}^{5-}$, $SiW_{11}O_{39}{}^{8-}$, $ZnSiW_{11}O_{39}{}^{6-}$, $NaP_5W_{30}O_{110}{}^{14-}$, etc.—for the selective aerobic oxidation of H_2S in aqueous solution to yield a high purity (>99.5%) sulfur. Selective oxidation of tetrahydrothiophene to the corresponding sulfoxide by O_2 was achieved in high selectivity (>99%) at 95 °C in the presence of HPA-2 as catalyst.[184] A range of POMs catalyze the selective oxidation of thioethers to the corresponding sulfoxides by *tert*-butyl hydroperoxide at 25 °C, HPA-2 being particularly selective (>99.9%).[185] A mechanism, including outer-sphere electron transfer from thioether to POM, is suggested.[185]

Another interesting field is the application of HPA-*n* redox catalysis for environmentally benign delignifying wood pulp.[186] Lignin—a complex polymer derived from aromatic alcohols—is, besides cellulose, one of the main constituents of wood. Delignification is a step in manufacturing paper. Currently, it is typically done by treatment of the pulp by chlorine at a low pH, which poses a great environmental concern. Weinstock, Hill et al.[186] have developed a new method of removing residual lignin from wood pulp consisting of oxidative degradation of lignin by POMs, e.g., HPA-2, followed by separation of bleached pulp and reoxidation of the reduced

POM by a nonpolluting oxidant, e.g., air, O_2, H_2O_2, etc. The process can be represented by eqs 23 and 24 where Red is now the pulp and Ox is the bleached pulp. The net reaction is the selective oxidative removal of lignin from wood yielding only high quality cellulose, CO_2 and H_2O:

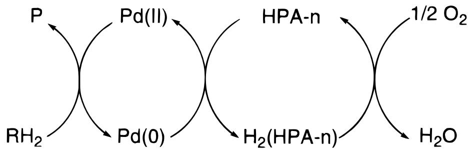
$$\text{wood (cellulose + lignin)} + O_2 \rightarrow \text{cellulose} + CO_2 + H_2O$$

As such, the method allows production of a paper-quality bleached pulp and is claimed to be an effective alternative to the chlorine bleaching.

Two-Component System HPA-n + Pd(II). The two-component redox system HPA-*n* + Pd(II)[1,156,187] has attracted considerable attention. A wide variety of stoichiometric oxidations of organic compounds (RH_2), e.g., olefins, alcohols, arenes, etc., by Pd(II) can be carried out catalytically with the use of HPA-*n* as a cocatalyst and O_2 as an oxidant[3,6,157,188] (eq 34).

$$RH_2 + {}^1/_2O_2 \rightarrow P + H_2O \tag{34}$$

Generally, such reactions proceed via a stepwise redox mechanism (eq 35).[1,3] It is analogous to the Wacker-type oxidation with $CuCl_2-PdCl_2$ as the catalyst. But the HPA-*n* + Pd(II) catalyst can work in the absence of or at a very low concentration of Cl^- ions. Consequently, it has the advantage of being higher selective and less corrosive.[1]



(35)

Most interesting is the application of the HPA-*n* + Pd(II) system for Wacker-type oxidation of olefins (eq 36):

$$RCH{=}CH_2 + {}^1/_2O_2 \rightarrow RCOCH_3 \tag{36}$$

The Wacker process is industrially employed for manufacturing acetaldehyde from ethylene and acetone from propylene.[189] The $CuCl_2$ + $PdCl_2$ redox system is used as a catalyst. However, this process has several drawbacks such as formation of chlorinated byproducts and strong corrosion of the reaction vessel. So the development of chloride-free oxidants to replace $CuCl_2$ has long been a challenge. Matveev[1,156,187] proposed the use of HPA-*n* as chloride-free oxidant in the Wacker reaction. The oxidation of ethylene can be represented by eqs 37−39.

$$C_2H_4 + Pd(II) + H_2O \rightarrow CH_3CHO + Pd(0) + 2H^+ \tag{37}$$

$$Pd(0) + HPA\text{-}n + 2H^+ \rightarrow Pd(II) + H_2(HPA\text{-}n) \tag{38}$$

$$H_2(HPA\text{-}n) + {}^1/_2O_2 \rightarrow HPA\text{-}n + H_2O \tag{39}$$

Table 7. Catalyst Solutions for Wacker Oxidation of Ethylene to Acetaldehyde[157]

catalytica's system		$CuCl_2$ + $PdCl_2$ system	
Pd(II)	0.1 mM	Pd(II)	10 mM
Cl^-	5−25 mM	Cl^-	2 M
$PMo_{10}V_2O_{40}{}^{5-}$	0.3 M	$CuCl_2$	1 M

Catalytica[157] has recently developed new technology for the Wacker oxidation of ethylene and higher olefins with the use of the HPA-*n* + Pd(II) system. In order to enhance the reaction rate and stabilize Pd(II) in solution, the reaction is still carried out in the presence of Cl^- ions, but at a very low concentration, much lower than in the conventional Wacker process (Table 7). In Catalytica's process, over 99% of the production of chlorinated byproducts is eliminated, decreasing to less than 0.01% yield on ethylene. The practical production of aqueous HPA-*n*, for use at large scale as well as in the laboratory, and the reoxidation of aqueous reduced HPA-*n* by O_2 has been described.[190]

Multicomponent Systems. Three-component redox system, including HPA-*n*, hydroquinone (HQ), and Pd(II), was found to be an efficient homogeneous catalyst for Wacker-type oxidation of alkenes.[191,192] In this system, HPA-*n* smoothly oxidizes HQ to benzoquinone; the latter is known[1] to rapidly oxidize Pd(0) to Pd(II), thus greatly enhancing the overall reaction rate. Addition of Cu(II) to the HPA-*n* + Pd(II) redox system can also benefit Wacker-type oxidation[193] (see below).

Pd(II) + HPA-*n* is an efficient homogeneous catalyst for the oxidative coupling of arenes (ArH) which is a useful route to the synthesis of biphenyl derivatives. For a review, see ref 194. Hg(II) is often

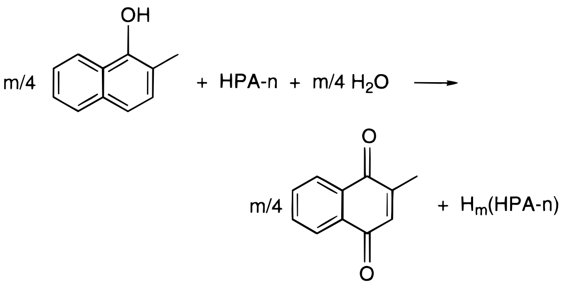
$$2ArH + {}^1/_2O_2 \rightarrow Ar{-}Ar + H_2O$$

employed as a promoter in the coupling of alkylbenzenes to improve activity and selectivity to 4,4'-isomers. Recently the oxidative coupling of methyl benzoate catalyzed by $Pd(OAc)_2$ + HPA-*n*, yielding 2,2'-biphenic acid dimethyl ester with unusually high selectivity (80%), has been reported.[195] An ortho cyclopalladated intermediate is suggested to be responsible for this. Addition of $Hg(OAc)_2$ increased greatly the conversion of methyl benzoate without impairing the selectivity to the 2,2′-isomer.[195]

3. Biphasic Oxidation

The advantage of biphasic systems is that they combine a catalytic reaction and product separation in one unit, allowing difficult separation problem to be avoided. Like in acid catalysis discussed earlier, polyoxometalates can be profitably used as catalysts for oxidation in biphasic systems.

Matveev et al.[196] reported two-stage oxidation of 2-methyl-1-naphthol to menadione in a high yield with space-separated steps (eqs 40 and 41). Step 40



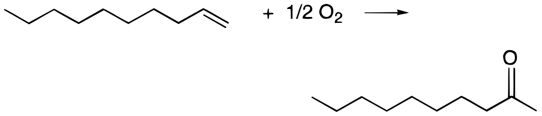
(40)

$$H_m(\mathrm{HPA}\text{-}n) + (m/4)O_2 \rightarrow \mathrm{HPA}\text{-}n + (m/2)H_2O \quad (41)$$

is carried out in a water−hydrocarbon two-phase system at 50 °C with 89% yield of menadione at a 100% naphthol conversion. This is a promising alternative to the conventional synthesis of vitamin K_3 by oxidizing 2-methylnaphthalene with CrO_3. 2-Methyl-1-naphthol can be produced in a high yield by a heterogeneously catalyzed gas-phase alkylation of naphthalene by methanol.

We[197] have developed the efficient one-stage oxidation of TMP to yield 84% TMBQ at a 100% TMP conversion in a two-phase system at 50 °C and 1 atm O_2 pressure (eq 32). The catalyst (lower) phase is a HPA-4 solution in $AcOH-H_2O$. The upper phase is a TMP + TMBQ solution in a hydrocarbon solvent, e.g., heptane, benzene, etc.

Monflier et al.[193] reported the biphasic Wacker oxidation of 1-decene to 2-decanone at 80 °C with excellent yield (98%) and practically no double-bond migration (eq 42). In this case, the catalyst (lower) phase is a three-component system, containing Pd(II), HPA-6, and Cu(II) in an aqueous solution, where Cu(II) is suggested to promote the Pd reoxidation. β-Cyclodextrin as a phase-transfer catalyst is used; apparently it transfers 1-decene to the aqueous phase by a host−guest interaction. However, no evidence on the integrity of β-cyclodextrin during the reaction course was provided.



(42)

4. Heterogeneously Catalyzed Oxidation

Heterogenized HPA-*n* catalysts have attracted considerable interest. Both liquid- and gas-phase reactions have been studied.

Liquid-Phase Oxidation. Neumann et al.[198] reported the liquid-phase oxidative dehydrogenation of benzylic alcohols and amines catalyzed by carbon-supported HPA-*n* in toluene at 100 °C with excellent yields (94−100%). The oxidation of benzylic alcohols to benzaldehydes (eq 43) proceeds without overoxidation to carboxylic acids. Reaction 44 proceeds via the oxidative dehydrogenation of benzyl amine to imine, ArCH=NH, followed by the hydrolysis of the imine to form benzaldehyde, and, finally, the interaction between the imine and benzaldehyde yields a Schiff base.

$$ArCH_2OH + {}^1/_2O_2 \rightarrow ArCHO + H_2O \quad (43)$$

$$ArCH_2NH_2 + O_2 \rightarrow ArCH{=}NCH_2Ar \quad (44)$$

Jansen[81] applied HPA-*n* ($n = 2, 3$) supported on a variety of chemically modified carbon supports as catalysts for the oxidation of TMP to TMBQ (eq 32) in polar media.

Ishii et al.[199] studied the aerobic oxidation of various organic compounds catalyzed by a carbon-supported (10%) NH_4^+ salt of HPA-*n* with the average composition $(NH_4)_5H_6PMo_4V_8O_{40}$. This catalyst showed high catalytic activity for the oxidative dehydrogenation of benzylic and allylic alcohols to the corresponding aldehydes and ketones (46−92% yield) in toluene. The catalyst can be recycled without loss of its activity. In contrast, the nonsupported catalyst was inactive for the same oxidation under the same conditions. The enhancement of catalytic activity by supporting POM on the active carbon is believed to be due to the higher concentration of substrates and oxygen by the adsorption in the vicinity of the active site. In addition, the active carbon could be a good mediator of the electron transfer in redox steps involved in the catalytic process. It should be noted, however, that the supported catalyst has greater surface area compared to the bulk POM, which may be the major reason for the greater activity of the supported system. Other aerobic oxidations, such as the oxidation of phenols and amines, have also been examined.[199] In the case of reactions in polar media a significant leaching of POM from the active carbon was observed. Thus in the oxidation of TMP to TMBQ (eq 32) in $AcOH-H_2O$, 7% of POM supported on active carbon eluted from the support in the solvent, which might give rise to the homogeneously catalyzed reaction. Although the recycled catalyst showed almost the same performance as the original one, it is not sufficient to exclude the homogeneous reaction. The best way to examine the role of homogeneous catalysis in a liquid−solid system is to check the activity of the filtrate obtained at the reaction temperature.

Gas-Phase Oxidation. Attempts have been made to apply a solid two-component Pd(II) + HPA-*n* system in the gas-phase Wacker oxidation and related reactions. These reactions have usually been carried out in the presence of steam. Mechanistically, they can be considered as pseudohomogeneous, i.e., occurring in the liquid catalyst phase entrapped in a support. As a support, silica is often used, which is relatively inert toward POM. Real mechanisms, however, may be more complex, but little data is available so far. There are two main problems in applying this system to the gas-phase oxidation: (1) the reoxidation of the catalyst by O_2 proceeds much slower than in solution and (2) the catalyst is rapidly deactivated probably due to aggregation of palladium.

The heterogeneous oxidation of butene to methyl ethyl ketone (eq 45) is a challenging goal.[200,201]

$$n\text{-}C_4H_8 + {}^1/_2O_2 \rightarrow CH_3CH_2COCH_3 \qquad (45)$$

Stobbe-Kreemers et al.[200] have studied this reaction catalyzed by the solid Pd(II) + HPA-*n* system at 70 °C. Not only HPA-*n* but also their Cu^{2+}, Ni^{2+}, Pd^{2+}, and Cs^+ salts have been used. A strong catalyst deactivation was observed: the conversion of butene dropped 10-fold from 60% to 6% after 1 h on stream, while the selectivity decreased less dramatically, only from 98% to 90%.

Recently, Nowinska et al.[202] reported quite a stable activity in the oxidation of ethylene to acetaldehyde with a Mn^{2+}-promoted catalyst, ($PdCl_2$ + Mn^{2+}+ HPA-2)/SiO_2. After 50 h on stream at 70 °C, a constant 98% selectivity at 80% ethylene conversion was observed. Without palladium, HPA-2 supported on silica or τ-alumina catalyzes the direct gas-phase oxidation of ethylene to acetic acid at 230 °C with about 50% selectivity at 55% conversion, CO_2 as the major byproduct being formed.[203]

Volkova et al.[204] reported that ($PdCl_2$ + HPA-6)/SiO_2 catalyzes the oxidation of methane and other alkanes by O_2 at 300 °C. Thus CH_4 is converted to CH_3Cl and CO_2 with selectivities of 20 and 25%, respectively. No reaction occurs without $PdCl_2$. HPA-6 is suggested to mediate the reoxidation of reduced palladium by O_2. The relative oxidation rate increases in the series of alkanes: CH_4 (0.14) < C_2H_6 (1.0) < C_3H_8 (2.0) < i-C_4H_{10} (2.2) < *n*-C_4H_{10} (3.4) < cyclopentane (6.8) = cyclohexane (6.8) < *n*-C_5H_{12} (7.2).[205]

The oxidation of CO to CO_2 catalyzed by supported Pd(II) + HPA-*n* catalysts was reported by Pavlova et al.[206] (eq 46):

$$CO + {}^1/_2O_2 \rightarrow CO_2 \qquad (46)$$

The (1.5% Pd(II) + 7.5% HPA-*n*)/SiO_2 catalyst was found to be more active than Pd/TiO_2 and Pd/SiO_2 at 30 °C. But eventually the catalyst was irreversibly deactivated.

5. Mechanism

Despite the importance and versatility of redox reactions catalyzed by HPA-*n*, there is only limited information about their mechanisms. HPA-*n* in solution is an extremely complex system, and the higher the *n* value, the more complex the system. The HPA-*n* solutions contain a great number of polyanions, their positional isomers as well as monomeric metallospecies.[3,157] Figure 9 shows the ^{31}P NMR spectrum for HPA-4 aqueous solution, which was used as the catalyst for oxidation of TMP to TMBQ.[197] As seen, this system contains heteropolyanions with one, two, three, and four V ions. Moreover, each type is represented by an array of positional isomers. Such a complexity makes mechanistic studies very difficult. Much work has been done on the characterization of the HPA-*n* solutions, going back to the studies by Souchay,[21,22] Pope,[19] and Matveev[1,3] and co-workers. Recently Pettersson et al.[207] have fully characterized the HPA-2 solutions by potentiometry and ^{31}P and ^{51}V NMR. This is a relatively simple and stable system, which is used in Catalytica's new technology for the Wacker oxidation of olefins.[157] Yet it consists of five positional α-isomers and some β-isomers of $PMo_{10}V_2O_{40}{}^{5-}$.

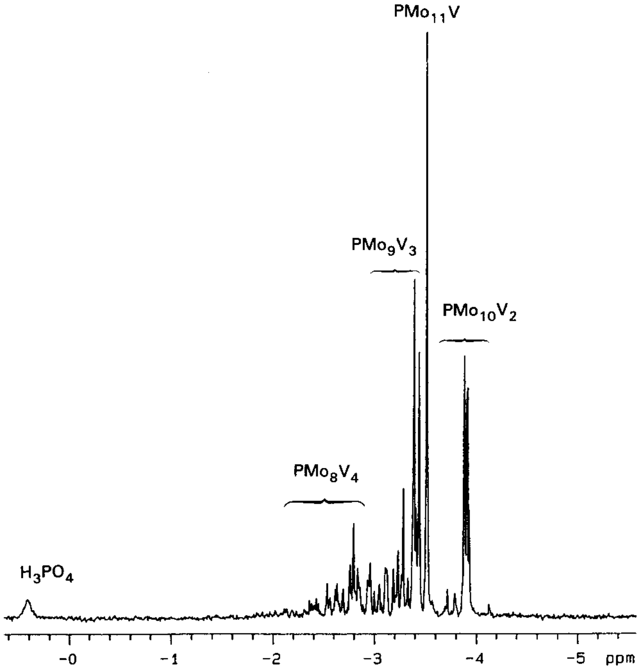


Figure 9. 162 MHz ^{31}P NMR spectrum for 0.2 M $Na_5H_2PMo_8V_4O_{40}$ aqueous solution (pH 2.5, 1% H_3PO_4 as external reference).

As stated earlier, the overall catalytic process can be represented schematically by steps 23 and 24. The question is what is the mechanism of these steps? What kind of active species is involved? In step 23, two types of active species can be considered—the monomeric VO_2^+ cation (and/or complexes thereof) and heteropolyanions.[3] The VO_2^+ cation is formed via the dissociation of parent HPA-*n* (eq 47). It is likely for HPA-*n* with higher *n* and in strongly acidic media. There is evidence that VO_2^+ is the active species in the oxidation of TMP (ArOH) to TMBQ (eq 32). The reaction mechanism can be represented by eqs 47–52.[180]

$$\text{HPA-}n \rightarrow VO_2^+ + \text{HPA-}(n-1) \qquad (47)$$

$$VO_2^+ + ArOH + H^+ \xrightarrow[\text{slow}]{} ArO^\bullet + VO^{2+} + H_2O \qquad (48)$$

$$ArO^\bullet \rightarrow \cdots \rightarrow TMBQ \qquad (49)$$

$$VO^{2+} + \text{HPA-}n + H_2O \rightarrow VO_2^+ + H(\text{HPA-}n) + H^+ \qquad (50)$$

or

$$VO^{2+} + \text{HPA-}(n-1) + H^+ \rightarrow H(\text{HPA-}n) \qquad (51)$$

$$4H(\text{HPA-}n) + O_2 \rightarrow 4\text{HPA-}n + 2H_2O \qquad (52)$$

Table 8. One- vs. Two-Electron Oxidation of *t*-Bu(Ph)CHOH[a,210]

oxidant	$PdCl_2$	Ce^{4+}	$S_2O_8^{2-}$	VO_2^+	$PMo_6V_6O_{40}^{9-}$
ketone, %	100	6	6	11	67
PhCHO, %	-	94	89	63	33

[a] Yields (mol %) on converted alcohol; a little PhCOOH also formed.

The rate-determining step is probably one-electron oxidation of the phenol by VO_2^+ to form phenoxyl radical and VO^{2+} (eq 48). Subsequent transformations of the phenoxyl radical give TMBQ. VO^{2+} either interacts with HPA-*n* by electron transfer (eq 50) or enters the lacunary species HPA-(*n*-1) (eq 51) to form the reduced heteropolyanion H(HPA-*n*). Eventually, H(HPA-*n*) is oxidized by O_2 (eq 52) by a multielectron-transfer mechanism which will be discussed later. It should be noted that the free VO^{2+} ion is not oxidized by O_2 in acidic solution.

Interestingly, the tungsten analogs of HPA-*n*, $PW_{12-n}V_nO_{40}^{(3+n)-}$, which are much less labile than $PMo_{12-n}V_nO_{40}^{(3+n)-}$ in aqueous solution,[208] showed a very low activity in the oxidation of TMP[180] as well as in some other reactions, e.g., in oxidation of H_2S.[209] A possible reason for this is that in the case of $PW_{12-n}V_n$, reactions 47 and 51 are too slow.

Besides VO_2^+, parent heteropolyanions can be the active species in step 23.[3] It is likely in the case of more stable polyanions with fewer V^{5+} ions (e.g., HPA-2). Since the heteropolyanions are multielectron oxidants, they can, in principle, react via a multielectron-transfer mechanism. In this sense, the oxidation of a test alcohol *t*-Bu(Ph)CHOH is of interest[210] (eq 53).

$$^{\bullet}C(CH_3)_3 + PhCHO \xleftarrow{-1e^-} PhCH(OH)C(CH_3)_3 \xrightarrow{-2e^-} PhC(=O)C(CH_3)_3 \quad (53)$$

With two-electron oxidants, e.g., Pd(II), this alcohol gives a ketone with the same carbon backbone. With one-electron oxidants, e.g., Ce^{4+} and persulfate, the C–C bond cleaves to yield benzaldehyde and *tert*-butyl radical as the primary products (Table 8). It is seen that VO_2^+ reacts as one-electron oxidant, as expected, yielding 63% benzaldehyde. In contrast, HPA-6 predominantly reacts as a two-electron oxidant, giving the ketone in 67% yield; simultaneously a one-electron oxidation, probably by VO_2^+ ions, also takes place to give benzaldehyde (33%). This may indicate a direct involvement of heteropolyanions in reaction 53.

Efforts have been made to clarify the mechanism of oxidation of the reduced form of HPA-*n* ("blue") by O_2 in solution (eq 24).[3,159] However, the complexity of the system makes conclusions rather speculative. Below are given redox reactions involved in the reduction of dioxygen in an acidic aqueous solution together with the corresponding redox potentials (versus NHE, pH 0).[211] These data allow to make a thermodynamic assessment as to how the oxidation of bues may proceed.

$$O_2 + e^- + H^+ \rightarrow HO_2 \qquad E = -0.05\ \text{V}$$

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \qquad E = 0.68\ \text{V}$$

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \qquad E = 1.23\ \text{V}$$

$$HO_2 + e^- + H^+ \rightarrow H_2O_2 \qquad E = 1.44\ \text{V}$$

$$H_2O_2 + e^- + H^+ \rightarrow HO + H_2O \qquad E = 0.71\ \text{V}$$

$$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O \qquad E = 1.76\ \text{V}$$

$$HO + e^- + H^+ \rightarrow H_2O \qquad E = 2.81\ \text{V}$$

It can be seen that O_2 is a rather poor one-electron oxidant. One-electron oxidation of the reduced HPA-*n* ($E = 0.7$ V) with O_2 to form HO_2 radical is highly unfavorable thermodynamically. However two-, three-, or four-electron oxidations are feasible. Consequently, the HPA-1 blue, $PMo_{11}V^{4+}O_{40}^{4-}$, is practically not oxidized by O_2 under mild conditions in solution. The all-molybdenum HPA-0 blue is not oxidized either. For these reasons, HPA-*n* with $n > 1$ are used as catalysts for liquid-phase oxidations. Note, however, that the reoxidation of HPA-0 and HPA-1 by O_2 proceeds readily at higher temperatures, >200 °C, which allows them to be applied under such conditions for gas-phase oxidations, e.g., the oxidation of methacrolein and oxidative dehydrogenation of isobutyric acid.[2,8,10,12]

Apparently, the mechanism of step 24 depends on the degree of reduction of the blue. The oxidation of a deeply reduced blue ($n \geq 4$, all the V present reduced to V^{4+}) follows a simple kinetics: first order in both the blue and O_2.[212] In the presence of a radical scavenger, *i*-PrOH, no acetone was found. This may indicate that no free radicals are formed during the reaction. (However, the formation of short lived free radicals is not excluded.) Hence a four-electron-transfer mechanism was proposed, including the formation of a complex between the blue and O_2 followed by a stepwise four-electron transfer therein (eq 54).[212] Each electron-transfer step is probably accompanied by the protonation of the oxidant.

$$H_m(HPA\text{-}n) + O_2 \rightarrow \{H_m(HPA\text{-}n)\cdots O_2\} \xrightarrow[\text{slow}]{(4e^-)} H_{m-4}(HPA\text{-}n) + 2H_2O \quad (54)$$

In contrast, the oxidation of a weakly reduced blue (by less than one electron per Keggin unit) shows a more complex behavior.[213] This system is adequate to a real one-stage process. For simplicity, it can be considered as one consisting of two species: one-electron blue, H(HPA-*n*), and HPA-*n*; [H(HPA-*n*)]/{[H(HPA-*n*)] + [HPA-*n*]} << 1. Under such conditions, the rate of oxidation of blues is in the sequence: HPA-2 < HPA-3 > HPA-4 > HPA-6. In the case of the HPA-3 blue, at a constant pH and ionic strength, the reaction was found to be third-order in H(HPA-*n*), minus second order in the HPA-*n* and first order in O_2. The test with *i*-PrOH clearly showed the formation of free radicals. On these bases, a mechanism was proposed, which is represented for the HPA-3 blue by eqs 55−58:

$$2PMo_9V_2^{5+}V^{4+} \rightarrow PMo_9V^{5+}V_2^{4+} + PMo_9V_3^{5+} \quad (55)$$

$$PMo_9V^{5+}V_2^{4+} + PMo_9V_2^{5+}V^{4+} \rightarrow PMo_9V_3^{4+} + PMo_9V_3^{5+} \quad (56)$$

$$PMo_9V_3^{4+} + O_2 + 3H^+ \xrightarrow[\text{slow}]{(3e^-)} PMo_9V_3^{5+} + H_2O + HO \quad (57)$$

$$PMo_9V_2^{5+}V^{4+} + HO + H^+ \rightarrow PMo_9V_3^{5+} + H_2O \quad (58)$$

In steps 55 and 56, a three-electron blue is formed by the fast electron exchange between one-electron blues. Then the three-electron blue is slowly oxidized by O_2 via a stepwise transfer of three electrons from the blue to O_2, accompanied by the protonation of the oxidant, to form HO radical, which is finally trapped by any V^{4+} species.[213]

Further, it was found that the free radicals generated in step 24 can, to some extent, affect the selectivity of the one-stage catalytic process.[214] But obviously, they will do no harm in the case of the two-stage process.

Several types of intermediate complexes between a reduced POM and O_2 have been suggested.[168,213,215] As HPA-*n* is labile, easily exchanging oxygen atoms in the polyanion with aqueous solution,[208] we proposed the formation of an adduct with the direct bonding of O_2 to the V^{4+} ion in the HPA-*n* blue by incorporating O_2 into a coordination vacancy at the V^{4+} ion.[213] Neumann and Levin[168] suggested a μ-peroxo intermediate involving two polyanions and dioxygen in the HPA-2 reoxidation. For tungsten blues, e.g., $SiW_{12}O_{40}^{5-}$, which are inert toward oxygen exchange, an association of O_2 with POM through the terminal or bridging oxygen atom in the Keggin structure, forming an ozonide-type adduct, or a 7-coordinate peroxo moiety was suggested.[215]

A mechanism involving a covalently bonded metal−oxygen intermediate would lead to O_2 incorporation into the polyanion. Recently Duncan and Hill[216] quantified by ^{17}O NMR the incorporation of ^{17}O from $^{17}O_2$ in the oxidation of reduced $W_{10}O_{32}^{4-}$, $P_2W_{18}O_{62}^{6-}$, and HPA-2 in CH_3CN solution. In the case of tungsten POMs, no ^{17}O incorporation into polyanion was found; nor did ^{17}O exchange occur between the POMs and solvent. All the ^{17}O is found in H_2O and H_2O_2 formed in the reaction. These data rule out the formation of covalently bonded metal−oxygen intermediates in the case of tungsten POM and are consistent with an outer-sphere electron transfer between O_2 and reduced POM.[216] Such a mechanism is, indeed, likely from the thermodynamic point of view for POMs such as $H_2W_{12}O_{40}^{6-}$, $W_{10}O_{32}^{4-}$, $SiW_{12}O_{40}^{4-}$, etc., having the redox potential $E \approx 0$ V.[215] In contrast, the case for HPA-2 is not clear as that for tungsten POMs. For HPA-2, the ^{17}O incorporation was measured in the HPA-2-catalyzed oxidation of 1,3-cyclohexadiene with $^{17}O_2$. In this system, some ^{17}O did incorporate into the POM as well as the ^{17}O exchange between the POM and solvent took place. The total POM enrichment represented 6% of all ^{17}O products. Kinetic measurements indicated that the ^{17}O enrichment mainly occurred by the ^{17}O exchange between the product $H_2{}^{17}O$ and POM. These data, too, may be considered as inconsistent with a covalent-bonded metal−oxygen intermediate.[216] However, if the oxidation in question were a radical chain process, reactions 23 and 24 would play only a minor role in the overall O_2 consumption. In this case, indeed, the ^{17}O exchange between POM and the product $H_2{}^{17}O$ would contribute the most to the ^{17}O enrichment of POM regardless of the mechanism of reaction 24.

Kozhevnikov and Kholdeeva[217] have studied the kinetics of a number of one-electron reactions between tungsten POMs or blues and various reductants or oxidants, respectively, including the oxidation of $SiW_{12}O_{40}^{4-}$ and $PW_{12}O_{40}^{3-}$ blues with O_2, by a stopped-flow technique. The reaction rates were found to be in good agreement with Marcus theory for outer-sphere electron transfer, which supports this mechanism for the oxidation of SiW and PW blues by O_2. Hiskia and Papaconstantinou[215] studied kinetics and mechanism of the oxidation of reduced tungsten POMs, such as $SiW_{12}O_{40}^{4-}$, $H_2W_{12}O_{40}^{6-}$, and $P_2W_{18}O_{62}^{6-}$, with dioxygen.

In conclusion, HPA-*n* is the efficient and versatile catalyst system for oxidizing by O_2. Several promising processes based on the HPA-*n* catalysis have been developed, e.g., the Wacker oxidation of olefins. However, many mechanistic details are yet to be disclosed.

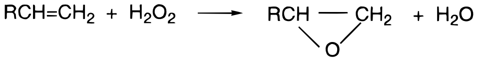
B. Oxidation with Hydrogen Peroxide

It has long been known that tungsten and molybdenum compounds are efficient catalysts for oxidations by hydrogen peroxide.[218,219] Tungsten and molybdenum POMs also 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.[16,154,220−225] Peroxo polyoxometalates have been shown to be the active intermediates in these reactions.[220−222]

1. Venturello–Ishii System

Two highly effective and mechanistically closely related catalyst systems relevant to POM-mediated hydroperoxide oxidation are of particular interest, namely, those developed by groups of Venturello and Ishii.

Venturello et al.[222,226,227] performed the epoxidation of alkenes (eq 59) in a biphasic system, e.g., $CHCl_3$−H_2O, at 60−70 °C with the use of diluted H_2O_2 (2−15%) and tungstate and phosphate ions as catalyst precursors in the presence of a phase-transfer catalyst—quaternary ammonium cation (Q^+) with C_6—C_{18} alkyl groups.


(59)

In this system, a peroxo POM, $\{PO_4[WO(O_2)_2]_4\}^{3-}$, analogous to the molybdenum peroxo POM first reported by Beiles et al.,[228] was isolated and characterized.[222] This peroxo complex was found to be remarkably effective in stoichiometric as well as in catalytic biphasic oxidation of alkenes by H_2O_2 and was postulated to be the active oxygen-transfer agent in reaction 59. For example, the epoxidation of 1-octene with 15% H_2O_2 in the presence of $\{PO_4[WO(O_2)_2]_4\}^{3-}$ in a $CH_2ClCH_2Cl-H_2O$ 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.[222] Likewise, but in a stronger acidic medium, the biphasic oxidation of alkenes produces 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). The glycols formed are present almost entirely in the aqueous phase and can be readily isolated from the reaction mixture.[227]

The anion $\{PO_4[WO(O_2)_2]_4\}^{3-}$ was characterized crystallographically (Figure 10).[222] It 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 $W(O_2)_2O_3$. Each tungsten atom is linked to two peroxo groups—one nonbridging (η^2) and the other bridging (η^2,η^1)—located in the equatorial plane of the pentagonal bipyramid.

Ishii et al.[224,229—238] demonstrated that oxidations of a wide variety of organic substrates with commercially available 35% H_2O_2 can be effectively performed in homogeneous phase or more often in a biphasic system with the use of a catalyst comprising heteropoly acids PW or PMo and cetylpyridinium chloride, the latter providing phase-transfer function. For a review, see ref 224. The PW catalyst is usually superior to PMo. Tris-cetylpyridinium salt of PW, $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3(PW_{12}O_{40})^{3-}$ (CPW), is prepared by interacting PW with 3 equiv of cetylpyridinium chloride. This salt catalyzes the epoxidation of alkenes[229] and allylic alcohols[233] with H_2O_2 in a biphasic system using $CHCl_3$ as the solvent, while α,β-unsaturated carboxylic acids are readily epoxidized in water at pH 6 to 7.[234] *sec*-Alcohols and diols are dehydrogenated by the $CPW-H_2O_2$ system in *tert*-butyl alcohol to give the corresponding ketones in good yields.[233] Primary alcohols are much less reactive under such conditions. However, α,ω-diols give lactones in fair yields.[224] The $CPW-H_2O_2$ system is also efficient for oxidative cleavage of carbon—carbon bonds of *vic*-glycols and alkenes to yield carboxylic acids.[233] Other reactions, which can be readily carried out with this system include the conversion of internal alkynes to the corresponding α,β-epoxy ketones,[236] allenes to α-alkoxy or α-hydroxy ketones,[237] amines to oximes and nitrones,[235] anilines to azoxy-, nitroso-, and nitrobenzenes[232] and sulfides to sulfoxides and sulfones.[238]

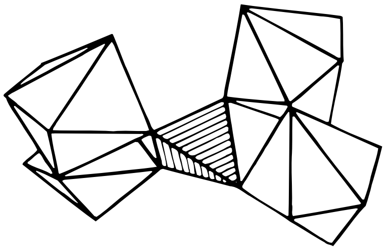


Figure 10. The structure of peroxo polyanion $\{PO_4[WO(O_2)_2]_4\}^{3-}$.[222]

According to a schematic mechanism proposed by Ishii et al,[224] the two-phase epoxidation of alkenes by hydrogen peroxide in the presence of $PW_{12}O_{40}{}^{3-}$ as the catalyst precursor proceeds as follows. An active peroxo POM is formed in the aqueous phase by interacting the Keggin heteropolyanion with hydrogen peroxide. With the phase-transfer catalyst, Q^+, the peroxo POM is almost fully transferred into the organic phase because its Q^+ salt is readily soluble in organic solvents. The reaction takes place preferentially in the organic phase via the oxygen atom transfer from the peroxo POM to the substrate. The peroxo POM is then regenerated at the interface by the interaction with H_2O_2. However, the nature of peroxo POM intermediates was not established in these studies.

In the recent years, the Venturello—Ishii chemistry has been investigated in detail by several groups.[239—249] These studies showed that the epoxidation of alkenes in the Venturello system and in the Ishii system includes nearly identical peroxo polyoxometalate intermediates despite the use of different catalysts precursors in the two systems. Csanyi and Jaky[239] demonstrated that PW_{12} and PMo_{12}, by the interaction with excess H_2O_2 in a two-phase system in the presence of a phase-transfer agent, decompose to form a variety of peroxo complexes including $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and $\{PO_4[MoO(O_2)_2]_4\}^{3-}$, respectively, which are transferred into the organic phase. These authors suggested that the peroxo anions derived from PW_{12} and PMo_{12} are the catalytically active species in the biphasic epoxidation of olefins. Brégeault et al.[240] studied the epoxidation of 1-octene by hydrogen peroxide in the $CHCl_3-H_2O$ system in the presence of the heteropolyanions $XM_{12}O_{40}{}^{n-}$ and $X_2M_{18}O_{62}{}^{m-}$ and isopolyanions $M_xO_y{}^{z-}$ ($M = Mo^{6+}$ or W^{6+}; $X = P^{5+}$, Si^{4+}, or B^{3+}) as precursors of catalytically active peroxo POM. The anions $BW_{12}O_{40}{}^{5-}$, $SiW_{12}O_{40}{}^{4-}$, and $P_2W_{18}O_{62}{}^{6-}$ were inactive and, as shown by a number of spectroscopic methods, did not change their structure during the reaction. $PMo_{12}O_{40}{}^{3-}$ exhibited a low activity. On the other hand, $PW_{12}O_{40}{}^{3-}$ exhibited a high activity (79% yield of epoxide based on 1-octene) when the catalytic system was prepared beforehand by interacting the heteropolyanion with H_2O_2 in aqueous solution in the absence of Q^+ and 1-octene. When all the reagents

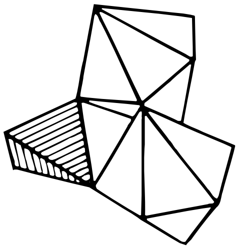


Figure 11. The structure of peroxo polyanion $\{HPO_4[WO(O_2)_2]_2\}^{2-}$.[241]

were mixed simultaneously, no activity was observed. Tungstic acid, "H_2WO_4", and $H_2W_{12}O_{42}^{10-}$ showed high activities regardless of the preparation method used, the yields being 76 and 67%, respectively. The Keggin heteropolyanions $PM_{12}O_{40}^{3-}$ were decomposed by excess H_2O_2 $\{[H_2O_2]/[M] = 30-355$ mol/mol$\}$ to form the peroxo POMs $\{PO_4[MO(O_2)_2]_4\}^{3-}$ and $[M_2O_3(O_2)_4(H_2O)_2]^{2-}$. It was suggested that $\{PO_4[MO(O_2)_2]_4\}^{3-}$ is the active species responsible for the olefin epoxidation with the Keggin anions $PM_{12}O_{40}^{3-}$ in two-phase systems.[240]

Later, ^{31}P and ^{183}W NMR study[241] showed that several peroxo POMs of the composition $PW_xO_y^{z-}$ ($x = 1-4$) form in the aqueous $H_3PW_{12}O_{40}/H_2O_2$ system, and these may well be the active species or their precursors in the olefin epoxidation by phase-transfer catalysis. The novel $\{HPO_4[WO(O_2)_2]_2\}^{2-}$ anion was studied in the crystalline state and in solution. The crystal structure of $[(n\text{-Bu})_4N]_2\{HPO_4[WO(O_2)_2]_2\}$ (Figure 11) is closely related to that of the Venturello complex $[(n\text{-Bu})_4N]_3\{PO_4[WO(O_2)_2]_4\}$ (Figure 10). The two anions, $\{HPO_4[WO(O_2)_2]_2\}^{2-}$ and $\{PO_4[WO(O_2)_2]_4\}^{3-}$, include the $[W_2O_2(\mu\text{-}O_2)_2(O_2)_2]$ moiety as a principal building block. In the two-phase epoxidation of limonene by H_2O_2, tungsten species $Q_3\{PO_4[WO(O_2)_2]_4\}$ and $Q_2\{HPO_4[WO(O_2)_2]_2\}$ proved to be 30 times more active than the molybdenum analog, $Q_3\{PO_4[MoO(O_2)_2]_4\}$.[241] Another mechanistically important result is that the $MO(O_2)_2$ moieties in $\{PO_4[MO(O_2)_2]_4\}^{3-}$ are remarkably mobile in solution. Thus mixing solutions of $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ at room temperature results in the fast formation of mixed-addenda species $\{PO_4[Mo_{4-x}W_xO_{20}]\}^{3-}$.[242] Thus, the whole array of peroxo species $PW_xO_y^{z-}$ ($x = 1-4$) is likely to exist in a fast equilibrium. This makes it difficult to identify the active species kinetically.

In the recent studies by Brégeault et al.[242,243] and Griffith et al.,[244-247] a wide variety of new mono-, di-, tri-, and tetranuclear tungsten and molybdemum peroxo POMs with η^2,η^1-peroxo moieties and various central groups—PO_4, $PhPO_3$, Ph_2PO_2, SO_4, AsO_4 $HAsO_4$, CH_3AsO_3, etc.—have been isolated and characterized by X-ray and tested in oxidations with H_2O_2. Schwendt et al. reported the synthesis and characterization of vanadium(V) peroxo complexes $(NH_4)_5[V_2O_2(O_2)_4PO_4]$[250] and $K_7[V_4O_4(O_2)_8PO_4]$.[251]

Ballistreri et al.[248] and Hill et al.[249] have shown that the Venturello–Ishii epoxidation is first-order in both $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and alkene. Hill et al.[249] obtained kinetic and spectroscopic evidence that two processes dominate during the reaction: a slow epoxidation by oxygen atom transfer from the peroxo POM to alkene (eq 60):

$$\{PO_4[WO(O_2)_2]_4\}^{3-} + \text{alkene} \rightarrow \text{PW}_4,\ \text{PW}_3,\ \text{and PW}_2 + \text{epoxide} \quad (60)$$

followed by a rapid regeneration of $\{PO_4[WO(O_2)_2]_4\}^{3-}$ with H_2O_2. Catalyst deactivation as well as the use of chlorinated hydrocarbons as solvents have been mentioned as the major drawback to the Venturello–Ishii process.[249]

In alkene epoxidation catalyzed by transition metal complexes, the mechanism of the oxygen atom transfer from a peroxo complex to alkene is still a matter of debate. According to Mimoun,[252] the mechanism of the oxygen-to-alkene transfer from a side-bonded η^2-peroxo group involves a precoordination of the alkene to the metal center. Alternatively, Sharpless[253] proposed a coordination of the alkene to one oxygen atom from the peroxo group, forming a three-center transition state. Although it is not easy to make a choice between the two, experimental results on mononuclear peroxo complexes are in a better agreement with the Sharpless mechanism.[254,255] This may well be the case with peroxo polyoxometalates, but no direct information is available.

Mechanistic aspects of the oxidation of *N*,*N*-benzylalkylamines to nitrones by $Q_3\{PO_4[MO(O_2)_2]_4\}$ (where M = Mo or W) have been studied.[256]

2. Other Polyoxometalate Systems

Polytungstometalates $[WM_3(H_2O)_2(XW_9O_{34})_2]^{12-}$ (X = M = Zn or Co^{2+}, which can be substituted by a variety of transition metal ions)[257] proved to be promising oxidation catalysts. These anions contain two α-β-$[XW_9O_{34}]^{12-}$ fragments of the Keggin-type polyanion $XW_{12}O_{40}^{6-}$ from which a triad of edge-sharing octahedra is removed. The two units are linked by four coplanar octahedrally coordinated and closely packed metal atoms. In contrast to Keggin anions, which are only stable in acidic solutions, these POMs are stable in the pH region from about 6 to about 10.[257] Atoms in the M positions can be substituted by Mn^{2+}, Mn^{3+}, $Fe^{2+,}$ Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+}, Pt^{2+}, V^{4+}, etc., thus providing intriguing opportunities for catalyst design. Apparently, these POMs are stable not only to hydrolysis but also to degradation by H_2O_2, unlike the Keggin ones. Thus Khenkin and Hill[258] reported that the $[Fe_4(PW_9O_{34})_2]^{10-}$ anion was quite stable with respect to solvolysis by H_2O_2; it catalyzed the selective homogeneous epoxidation of alkenes in aqueous acetonitrile at 20 °C by H_2O_2.

According to Neumann et al.,[259,260] solvolytically stable disubstituted manganese(II) POM, $[WZnMn_2(H_2O)_2(ZnW_9O_{34})_2]^{12-}$, is highly active catalyst for the epoxidation of alkenes and oxidation of alcohols by 30% H_2O_2 (only a small excess) in a biphasic system at ambient temperature, with very high selectivities (>99%) and hundreds to thousands of turnovers. Interestingly, trisubstituted POM, $[WMn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$, was significantly less efficient, followed by Zn^{2+} and Co^{2+} derivatives. The Rh^{3+} POM, $[WZnRh_2(H_2O)_2(ZnW_9O_{34})_2]^{10-}$, is about as effective as the disubstituted Mn^{2+} analog.[261] Other substrates, e.g. alkenols, diols, amines, etc., can be oxidized in such systems.[262]

POM-based solid catalysts for the epoxidation of alkenes have been reported.[263] These contain POM—$\{PO_4[WO(O_2)_2]_4\}^{3-}$ or $[WZnMn_2(H_2O)_2(ZnW_9O_{34})_2]^{12-}$—immobilized on a silicate xerogel covalently modified with phenyl groups and quaternary ammonium groups. The catalysts epoxidize alkenes by 30% H_2O_2 at room temperature in the absence of an organic solvent.

The Ti-substituted Keggin-type anions, $PW_{11}TiO_{40}{}^{5-}$, $PW_{10}Ti_2O_{40}{}^{7-}$, etc., have been studied as catalysts for the epoxidation of alkenes with H_2O_2. The kinetic data obtained imply the involvement of HO radicals generated by the decomposition of H_2O_2.[264]

Keggin-type mixed-addenda heteropolyanions containing V^{5+} ions catalyze the oxidation of alkylaromatic compounds by 30% H_2O_2 in AcOH at 80 °C to form the respective acetates or alcohols and aldehydes or ketones, HPA-2 being the most effective catalyst.[265] There is spectroscopic evidence that HPA-2 is not degraded during the reaction. However, there is a significant decomposition of H_2O_2 accompanying the oxidation of the alkyl aromatic substrates. The mechanism proposed includes the homolytic cleavage of peroxo species at the vanadium atom of HPA-2 to form HO and HO_2 radicals, which react with the alkyl aromatic substrate to give the observed products, as represented by eqs 61−65.[265]

$$\text{HPA-2} + H_2O_2 \rightarrow \text{H(HPA-2)} + HO_2 \qquad (61)$$

$$\text{H(HPA-2)} + H_2O_2 \rightarrow \text{HPA-2} + HO + H_2O \qquad (62)$$

$$ArH + HO\ (\text{or } HO_2) \rightarrow Ar^{\bullet} + H_2O\ (\text{or } H_2O_2) \qquad (63)$$

$$Ar^{\bullet} + \text{HPA-2} + H^+ \rightarrow Ar^+ + \text{H(HPA-2)} \qquad (64)$$

$$Ar^+ + AcOH\ (\text{or } H_2O) \rightarrow ArOAc + H^+\ (\text{or } ArOH) \qquad (65)$$

The molybdovanadium isopoly acids $H_2V_{12-x}Mo_xO_{31}$ ($x = 0-4$) catalyze the oxidation of 1,2,4-trimethylbenzene to trimethylbenzoquinone by peracetic acid in acetic acid solution (20 °C, 4 h) with a 12−31% selectivity at 15−22% trimethylbenzene conversion.[266]

As shown by Shimizu et al.,[267] 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. The mechanism proposed involves the HPA-catalyzed hydroxylation of the aromatic ring to form 2,3,5-trimethylhydroquinone, followed by its fast oxidation to TMBQ. In this reaction, HPAs apparently behave as Brönsted acid catalysts, catalyzing the formation of peracetic acid, which is probably the true hydroxylating species.[267] *vic*-Diols were oxidized with 30% aqueous H_2O_2 in the presence of HPA to yield carboxylic acid.[268]

Tungsten POMs have been studied as catalysts for the oxidation of benzene to phenol with 30% aqueous H_2O_2 at 25 °C by Nomiya et al.[269] Keggin anions, $PW_{10}V_2$ and PW_9V_3, showed 92−98% selectivity to phenol (based on benzene) at <8% benzene conversion. The activity of PW_9V_3 was initially high, but decreased after 48 h due to decomposition of the Keggin structure. The $PW_{10}V_2$ anion remained intact and maintained its activity even after 576 h. Kuznetsova et al.[270,271] reported that the Fe^{3+}-substituted POM, $PW_{11}O_{39}Fe^{4-}$, catalyzes the oxidation of benzene to phenol by H_2O_2 in CH_3CN solution at 70 °C, with the H_2O_2 decomposition being the main reaction. A mechanism, including the oxidation of C_6H_6 by HO radicals formed via the H_2O_2 decomposition, is suggested. Pd(II) and Pt(II) complexes of $PW_{11}O_{39}{}^{7-}$ catalyze the cooxidative hydroxylation of benzene to phenol by a gas mixture of O_2 and H_2 in a two-phase system at 10−40 °C.[272] Liquid-phase oxidation of benzene to phenol by O_2 (10 atm, 25 °C) in the presence of $Fe^{2+} + PW_{12}$ has been reported. [273] This reaction is likely to be a free radical cooxidation of a Fe^{2+}-POM and benzene by O_2. The benzene-to-phenol oxidation by O_2 catalyzed by the Pd(II) + HPA-*n* redox system has been reported to achieve a 70% selectivity to phenol at 15% benzene conversion and 800 Pd(II) turnovers (130 °C, 60 atm O_2, in AcOH−H_2O).[274]

POM-catalyzed oxidation of sulfur compounds with H_2O_2 may be promising for desulfurization of oils. Thus the oxidation of dibenzothiophene with H_2O_2 using PW as catalyst and $(C_8H_{17})_4NBr$ as phase transfer agent in a two-phase water−toluene system yields nearly 100% of dibenzothiophene sulfone. Treatment of gas oils with this method shows that all the sulfur compounds present are oxidized by this catalyst system. Oxidized products can be separated from oil by adsorption on silica gel. [275]

IV. Conclusion

Catalysis with heteropoly acids and related polyoxometalate systems is a field of growing importance. Several industrial processes based on HPA catalysis have been developed and commercialized. More may be launched in the years to come. The selected examples reviewed show the broad scope of potentially promising applications of HPAs as acid and redox catalysts in low-temperature liquid-phase organic reactions. Due to their unique physicochemical properties, HPAs can be profitably used in homogeneous, biphasic, or heterogeneous systems, providing a broad operational choice. In many cases HPAs provide higher activities and selectivities and allow for cleaner processing compared to conventional catalysts. The high effectiveness of HPAs as acid catalysts is primarily due to their strong Brönsted acidity, greatly exceeding that of ordinary mineral acids and solid acid catalysts. Such important HPA properties as the ability of polyanions to stabilize organic intermediates, "pseudoliquid phase" and lack of side reactions like sulfonation, etc., also contribute to enhancing the catalytic activity and reaction selectivity. In liquid-phase oxidation, polyoxometalates can be applied either as stoichiometric oxidants or as catalysts in conjunction with such environmentally friendly oxidants as O_2 and H_2O_2. The use of a variety of multicomponent redox systems based on polyoxometalates greatly extends the scope of possible oxidations. However, for these potentially promising reactions to be used in practice, complete recovery and recycling of HPA catalysts will be required. Detailed knowledge of mechanisms of catalysis by polyoxometalates is needed for the catalyst design and scale up.

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