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Fine organic synthesis with the aid of heteropolycompounds

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Contents

I. Introduction	473
II. Acid catalysis	473
III. Liquid-phase oxidation reactions	482
IV. Conclusion	487

Abstract. The use of heteropolycompounds (heteropolyacids and their salts) as acid and oxidation catalysts of fine organic synthesis reactions is examined. The use of heteropolycompounds in the synthesis of antioxidants, medicinal preparations, vitamins and other products produced on a small scale is discussed. Examples of the practical application of catalysis by heteropolycompounds are presented. The bibliography includes 177 references.

I. Introduction

Catalysis by heteropolycompounds (HPC) is one of the important aspects of the modern science of catalysis.[1–9] Studies in this field have been already prosecuted vigorously for 20 years. They permitted significant progress in the understanding of the mechanism of the catalytic effect of HPC at the molecular level and have led to the creation of a series of new industrial processes.

HPC have unique physicochemical properties. Catalysts based on them have a definite and well established structure. HPC catalyse effectively both acid-dependent and oxidation reactions and are frequently superior in their activity and/or selectively to known analogues.[2–4, 6] Their likely usefulness is indicated, in particular by the development and application in Japan of a series of new large-scale organic synthetic processes in which HPC are employed as catalysts (Table 1).[7] These processes include the oxidation of methacrolein to methacrylic acid, the hydration of olefins to alcohols, and polymerisation of tetrahydrofuran with ring opening (a stage in the synthesis of polyurethanes).

The use of HPC as catalysts of fine organic synthetic processes is very promising. By virtue of the high price of the products, the gain in selectivity as a result of the introduction of a more effective catalyst frequently covers severalfold the cost of the catalysts. Numerous studies have been carried out recently on the application of HPC as antioxidants, medicinal preparations, vitamins, biologically active substances, etc. There exist numerous patents for the application of HPC in fine organic synthesis. Some developments have already been applied in practice. The discussion of these new data is in fact the principal aim of the present review. The review is addressed primarily to synthetic chemists in order to draw their attention to the considerable possibilities which have arisen as a result of the application of HPC in synthetic practice. Attention is concentrated on acid-dependent and oxidation reactions of organic molecules in the liquid phase in homogeneous and heterogeneous systems. Certain new data concerning the preparation and properties of HPC-based catalysts are also considered. More complete information about the synthesis and the physicochemical and catalytic properties of HPC may be found in monographs and reviews.[1–14] The catalytic properties of HPC have been examined in greatest detail in a recently published review.[2]

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II. Acid catalysis

HPC are representatives of the large class of polynuclear complexes which combines a multiplicity of compounds differing in chemical composition and structure.[13] Despite their wide variety, until recently only the most stable and well investigated HPC have been used almost exclusively in catalysis. They contain the heteropolyanions $XM_{12}O_{40}^{x-8}$, where X is the central atom (Si^{4+}, P^{5+}, etc.), x is its oxidation state, and M is the metal ion (Mo^{6+}, W^{6+}, V^{5+}, etc.). The cations may be protons, metal ions, etc. These HPC have the well known Keggin structure (Fig. 1),[15] which includes the XO_4 tetrahedron surrounded by 12 MO_6 octahedra with common vertices and edges. Subsequently, for specially stipulated cases, HPC will be understood as compounds having this structure.

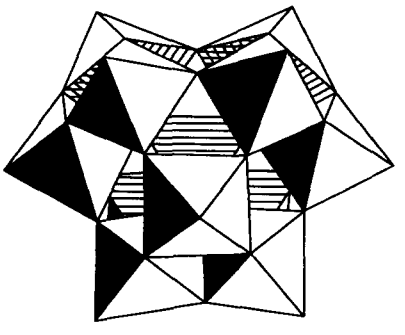


Figure 1. The structure of the heteropolyanion $XM_{12}O_{40}^{x-8}$ (α-isomer).[15]

Mainly the heteropolyacids $H_{8-x}[XM_{12}O_{40}]$ (HPA) are used in acid catalysis. Their high effectiveness as acid catalysts is due to a number of causes. In the first place, they are strong Brønsted acids, stronger than many of the usual acids employed as catalysts.[4] Heteropolyacids are readily soluble in water and

Table 1. Industrial heteropolyacid-catalysed processes.[7]

Reaction	Catalyst	Scale of industrial production/tonnes	Year of introduction
$CH_2=C(CH_3)CHO \xrightarrow{O_2} CH_2=C(CH_3)COOH$	Mo–V–P–HPA	95000	1982
$CH_2=C(CH_3)_2 \xrightarrow{H_2O} (CH_3)_3COH$	$H_3PMo_{12}O_{40}$	56000	1984
$CH_3CH=CHCH_3 \xrightarrow{H_2O} CH_3CH(OH)CH_2CH_3$	$H_3PMo_{12}O_{40}$	40000	1985
 $\xrightarrow{H_2O}$ $HO\text{-}(CH_2)_4\text{-}O\text{-}_n H$	$H_3PW_{12}O_{40}$	–	1987

oxygen-containing solvents and their thermal stability is high in the solid state. Because of this, they are used as both homogeneous and heterogeneous catalysts. Being 'soft' bases, heteropoly-anions (HPAN) are capable of effecting the specific coordination of the molecules of organic reagents, which may activate the latter in particular chemical reactions.[6, 7] The inertness of heteropoly-anions in relation to many side reactions, characteristic of organic reagents, which readily occur in the presence of the usual inorganic acids (sulfonation, chlorination, etc.), is important for homogeneous catalysis.[4] Because of the lability of their crystal structures and the high mobility of protons, solid heteropolyacids are capable of effecting not only the usual catalysis involving the active centres on their surface but they can also participate in bulk-phase catalytic action, like concentrated solutions of acids ('pseudoliquid phase').[6]

Data concerning the acid properties of heteropolyacids and their applications in acid catalysis have been examined in a number of reviews.[2, 4, 6]

1. Preparation of the catalysts

Heteropolyacids such as $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_3PMo_{12}O_{40}$ are used industrially in Russia and abroad in the form of hydrates. They are readily available. They are usually obtained by acidifying an aqueous solution containing the sodium salt of the heteroelement and sodium tungstate or molybdate and are isolated by extraction with ether.[10, 13, 14] Certain heteropoly-acids, in particular $H_3PMo_{12}O_{40}$ and mixtures of heteropolyacids having the composition $H_3PO_4 \cdot nMoO_3$ ($n = 6-9$), can be obtained by the direct reaction of the corresponding acids and oxides in solution without extraction with ether.[14, 16–18]

New possibilities in the synthesis of heteropolyacids have been provided by electrodialysis. This method makes it possible to obtain many heteropolyacids in quantitative yields from sodium salts.[19–25] An effective electromembrane method of synthesis of $H_3PW_{12}O_{40}$ by the reaction of Na_2WO_4 with H_3PO_4 in aqueous solution followed by the removal of Na^+ with the acid of a selective cation-exchange membrane has been developed and applied in industry.[22–24] The method is illustrated schematically in Fig. 2.

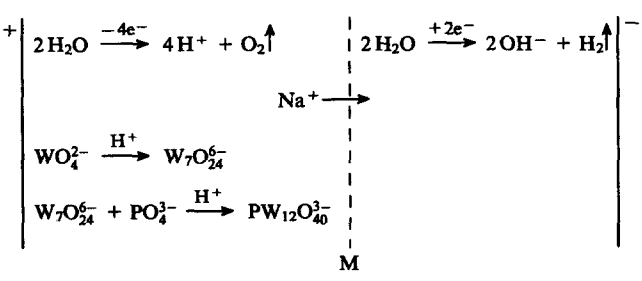


Figure 2. Schematic illustration of the synthesis of $H_3PW_{12}O_{40}$ with the aid of electrodialysis. M = cation-exchange membrane.

The $PW_{12}O_{40}^{3-}$ anion is formed in the anodic compartment of the electrodialyser from WO_4^{2-} and PO_4^{3-} taken in virtually stoichiometric proportions. The necessary acidification of the solution is achieved by electrolysing water. Heteropolyacids are synthesised in two stages.[21–24] In the first stage, in the absence of phosphate ions, WO_4^{2-} is converted into the isopolytungstate $W_7O_{24}^{6-}$. H_3PO_4 is then introduced and the electrochemical process is continued until completion. Under the influence of electric potential, Na^+ ions migrate from the anodic to the cathodic compartment through the cation-exchange membrane. This results in the concentration of aqueous $H_3PW_{12}O_{40}$ and NaOH solutions in the anodic and cathodic compartments respectively. The solution of the heteropolyacid is concentrated and the solid acid is crystallised out. Alkali is used to obtain Na_2WO_3 from WO_3 or H_2WO_4. Thus the process is waste-free. The yield of the heteropolyacid is close to 100% relative to tungsten. The Na^+ content in the final product does not exceed 0.01 wt.%. Other heteropolyacids, for example, $H_4SiW_{12}O_{40}$, $H_5PW_{11}TiO_{40}$, $H_5PW_{11}ZrO_{40}$, $H_6PW_{11}BiO_{40}$, $H_5PW_{11}CeO_{40}$, $H_6P_2W_{21}O_{17}$, and others, can be obtained similarly.[19, 21, 25]

As a rule, the tungsten acids are the best acid catalysts in the series of heteropolyacids. This is due to their greater acidity, resistance to hydrolysis, and thermal stability and also their lower oxidation potential compared with molybdic and vanadic acids.[4] However, cases are known also where Mo-HPA are used, for example, in industrial olefin-hydration processes.[7]

Massive heteropolyacids have a low specific surface ($1-5\ m^2\ g^{-1}$)[4, 26, 27] and are readily soluble in water and oxygen-containing organic solvents but are insoluble in hydrocarbons. The specific surface of insoluble salts, for example $Cs_{3-x}H_xPW_{12}O_{40}$,[28, 29] is $100-200\ m^2\ g^{-1}$. The porous structure of HPC has been examined.[30] Tungsten heteropoly-acids are stable up to ~400 °C.[31] The thermal stability of salts of heteropolyacids is higher than that of the acids themselves.

The strength and number of the acid centres of the hetero-polyacid can be regulated by selecting the outer-sphere cation, by replacing the central atom and the metal atom in the structure of the polyanion, and also by using carriers of different nature and by changing the concentration of the heteropolyacid on the latter.[4]

The disposition of heteropolyacids on inert carriers makes it possible to increase their surface area, but the strength of the acid centres is then somewhat reduced.[32] The deposited heteropoly-acids are usually obtained by impregnating or adsorbing the heteropolyacids from solutions on carriers. The adsorption of heteropolyacids from solutions in various solvents on silica gel, alumina, and activated charcoal has been investigated.[32, 33]

Silica gel is most often used as the carrier for the heteropolyacid in acid catalysis, whilst activated charcoal is more rarely employed; more basic carriers such as Al_2O_3 and MgO reduce the acidity of the heteropolyacid.[4, 34–36] When the heteropolyacid is deposited on SiO_2, its structure is retained.[34] According to X-ray diffraction data,[32, 34] a crystalline phase of the heteropolyacid appears on SiO_2 when the heteropolyacid content is >20%. Three forms of $H_4SiW_{12}O_{40}$ have been observed on the

Table 2. Dissociation constants of heteropolyacids 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	+	+

SiO_2 surface by electron microscopy: isolated heteropolyacid molecules, 50 Å clusters, and 500 Å crystallites.[32] The ratios of these forms depend on the amount of deposited heteropolyacid.

Catalysts obtained by depositing the heteropolyacid on its insoluble isostructural salt, for example, $H_{3+n}PMo_{12-n}V_nO_{40}/K_3PMo_{12}O_{40}$ ($n = 0-3$) have attracted interest recently.[37, 38] Such systems have an increased thermal stability. They are apparently analogous to the insoluble acid salts of the type $Cs_{3-x}H_xPW_{12}O_{40}$.[28, 29]

Heteropolyacid-based catalysts are activated before use by thermal dehydration. For the complete removal of water from the heteropolyacid, it is sufficient to heat it *in vacuo* at 200–250 °C for 1–2 h.

2. Acid properties of heteropolyacids

Heteropolyacids are strong Brønsted acids,[1-9] whilst heteropolyanions are 'soft' weakly solvated bases.[39] In solutions, heteropolyacids are stronger than many usual inorganic acids such as H_2SO_4, HCl, HBr, HNO_3, etc. (Table 2). The strength of heteropolyacids with the Keggin structure depends only slightly on their composition. However, tungsten heteropolyacids are appreciably stronger than molybdenum heteropolyacids. The strongest and the most stable among the acids of the M_{12}-series is $H_3PW_{12}O_{40}$.[4] The dissociation constants of heteropolyacids in water,[40, 41] acetone, ethanol, and acetic acid[42, 43] and their Hammett acidity functions in water and water–acetic acid, water–dioxane, water–ethanol, and water–acetone mixtures[44, 45] have been measured. The activities of water in $H_3PW_{12}O_{40}$ solutions have been determined.[44]

Solid heteropolyacids exhibit purely Brønsted acidity[46, 47] and are stronger than traditional acid catalysts such as aluminosilicates, H_3PO_4/SiO_2, and HX and HY zeolites.[46] The acidity of massive and deposited heteropolyacids has been investigated by various methods. These include the indicator method,[48, 49] measurement of diffusion coefficients[50] and ionic conductivities,[49, 51] ion exchange,[52] thermal desorption of bases,[46] IR spectroscopy,[34, 46, 47, 53] broad band ^1H NMR[11, 31, 54, 55] and ^1H NMR (MAS),[56, 57] ESCA,[58] etc.

According to adsorption calorimetric data,[59] the protic centres of $H_3PW_{12}O_{40}$ are fairly homogeneous (Fig. 3) and their strength is close to that of H-mordenite.† After deposition on silica gel (20% HPA/SiO_2), the protic centres are weakened, their strength approaching that of the protic centres of the HX and HY zeolites, and the centres become less homogeneous.[59] The strength of the acid centres of the deposited $H_3PW_{12}O_{40}$ diminishes in the sequence of carriers $SiO_2 > Al_2O_3 >$ activated charcoal (Sibunit).[59] The cause of the reduced acidity of the heteropolyacids on charcoal is so far obscure.

The structure of the protic centres of heteropolyacid-based catalysts has been studied.[4]

Neutral salts of heteropolyacids are also used in acid catalysis because they are capable of forming protic centres on interaction with the reaction medium.[2, 4, 6] Two mechanism of the generation

† Centres on which the heat adsorption of ammonia exceeded 90 kJ mol^{-1} were classified as protic.[59]

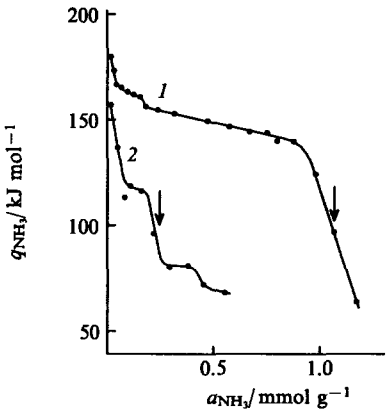


Figure 3. Differential heats of adsorption of NH_3 on $H_3PW_{12}O_{40}$ (*1*) and 20% $H_3PW_{12}O_{40}/SiO_2$ (*2*) at 150 °C. The position on the abscissa axis corresponding to the numbers of protic centres in the specimens are designated by arrows.[59]

of protic centres in heteropolyacid salts are distinguished[2, 6] — hydrolytic (for salts with the Al_3^+, Zn_2^+, etc. cations) and oxidation-reduction (for Cu^{2+}, Pd^{2+}):

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

$$Ag^+ + \frac{1}{2}H_2 \longrightarrow Ag^0 + H^+ .$$

The HPC containing simultaneously outer-sphere protons and transition metal cations are capable of acting as bifunctional catalysts. The hydroisomerisation of alkanes[2] on (Pt, Pd)/$H_3PW_{12}O_{40}$ may serve as an example.

The nature, strength, and number of acid centres can be regulated specifically by varying the chemical composition of the HPC, the type of carrier, the concentration of the HPC on the carrier, the conditions in the preliminary treatment of the catalyst, etc. The Keggin structure is retained over a wide range of acid properties of the HPC, which has been established reliably by spectroscopic methods (IR, ^{31}P, ^{17}O, ^{95}Mo, ^{183}W, ^{51}V, etc. MNR).[4, 11, 13] Because of these valuable properties, HPC are of great interest both for applied acid catalysis and as model systems for the study of fundamental problems of catalysis at the molecular level.

3. Mechanisms of acid catalysis by heteropolyacids

a. Homogeneous catalysis

The mechanism of the homogeneous acid catalysis by heteropolyacids is in principle similar to the mechanism of the catalysis by solutions of inorganic acids. In the simplest case, it can be represented schematically as follows:

$$S + HA \rightleftharpoons SH^+ + A^- ,$$

$$SH^+ \xrightarrow[(A^-)]{} P + HA ,$$

where S is the substrate, HA the catalyst, and P the product. Being stronger, heteropolyacids are capable of protonating the substrate and activating it for subsequent chemical reactions more effectively than the usual inorganic acids. As a result of this, heteropolyacids are as a rule much more active than inorganic acids.

Organic reactions in the presence of heteropolyacids and inorganic acids usually obey the same rules. Many examples of the parallel variation of the catalytic activity of heteropolyacids and their dissociation constants (the Brønsted equation) are known.[2, 4] In concentrated solutions of heteropolyacids, the rate

constant is found to depend on the Hammett acidity function H_0.[45, 60] Thus the rate constants for the hydration of isobutene in aqueous solution in the presence of $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ at 25 °C obey the equation[60]

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

The same relation holds for H_2SO_4, HCl, HNO_3, and $HClO_4$. On this basis, it has been suggested[60] that the hydration of isobutene in the presence of heteropolyacids and inorganic acids proceeds via the generally accepted mechanism in which the rate-limiting stage is the conversion of the π-complex between the olefin and H^+ into a carbonium ion.

$$(CH_3)_2C{=}CH_2 \overset{H^+}{\rightleftharpoons} (CH_3)_2C^{+}{-}CH_2 \longrightarrow (CH_3)_3C^+ \xrightarrow{H_2O} \longrightarrow (CH_3)_3COH + H^+ .$$

At the same time, the mechanisms of the catalytic action of heteropolyacids and inorganic acids in solutions differ somewhat, which is associated with the greater degree of dissociation of heteropolyacids and the high charge on the heteropolyanions. This is manifested primarily by a strong salt effect, which is observed in ionising media, for example, in water.[45, 60] This is indicated by the variable order of the reaction with respect to the catalyst, exceeding unity. Thus the formal order of the isobutene hydration reaction with respect to the heteropolyacid in dilute solutions (0.02–0.1 M heteropolyacid) is 1.2–1.5, while in concentrated solutions (up to 0.5 M) it is 2.0–2.2.[60] In the presence of inorganic acids, the reaction is virtually first-order. The contribution of the salt effect to the rate constants for the reactions of a non-electrolyte with an ionic reagent can be estimated with the aid of the Sechenov equation. In the case of bimolecular reaction, we have

$$\lg k = \lg k_0 + (B - B^{\neq})[H^+],$$

where k is the second-order rate constant at the given concentration $[H^+]$, $k_0 = k$ at $[H^+] = 0$, and B and $B^{\neq}$ are the salting-out coefficients in the ground and transition states.[60] This equation holds satisfactorily in the hydration of isobutene in the presence of both heteropolyacids and inorganic acids. Hence it was concluded that the true order of the reaction with respect to the heteropolyacid unity, as in the case of inorganic acids, and that its increase with increase in the concentration of the heteropolyacid is due to the salt effect.[60] The values of k_0, B, $B^{\neq}$, and $B-B^{\neq}$ for the hydration of isobutene in the presence of

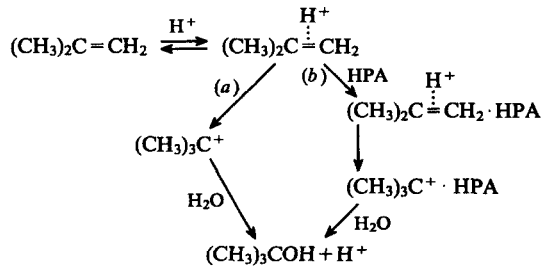
	$10^4 k^0$ / litre mol^{-1}	B / litre mol^{-1}	$B^{\neq}$ / litre mol^{-1}	$B-B^{\neq}$ / litre mol^{-1}
$H_3PW_{12}O_{40}$	20.0±3	−0.87	−3.0	2.1
$H_4SiW_{12}O_{40}$	17.0±4	−0.87	−3.0	2.1
HNO_3	3.8±0.4	−0.02	−0.2	0.2
H_2SO_4	5.0±1	+0.08	−0.2	0.3

different acids (at 25 °C) are given below:[60]

Evidently the constants k_0, extrapolated to $[H^+] = 0$, correspond approximately to the basicities of the acids, i.e. the rates of reaction per proton are similar regardless of the type of acid catalyst. Judging from the negative values of B and $B^{\neq}$, 'salting-in' i.e. a decrease in the level of the free energy of the ground and transition states due to the salt effect, almost always occurs. As was to be expected, the more polar transition state is 'salted-in' to a greater extent under these conditions. The fact that the salt effect $B-B^{\neq}$ is an order of magnitude higher for HPA than for inorganic acids is striking. This can be explained satisfactorily by the expected influence of ionic strength on the rate of the interaction of the polar molecule with an ion, because on complete dissociation of a 1–4 electrolyte ($H_4SiW_{12}O_{40}$) the ionic strength is ten times greater than on dissociation of a 1–1 electrolyte (HNO_3).

The kinetics of polar reactions involving ionic reagents are usually investigated in solutions with a fairly high constant ionic strength established by the addition of a neutral electrolyte in order to compensate for the salt effect. We may note that in the case of heteropolyacids the strong salt effect frequently renders this procedure relatively ineffective and this complicates the determination of the true order of the reaction with respect to HPA.

A number of workers have postulated the ability of 'soft' heteropolyanions to effect the specific coordination of organic molecules.[6, 7] Thus, a detailed study[2] of the hydration of isobutene in the presence of heteropolyacids made it possible to interpret the high order of the reaction with respect to the heteropolyacid on the hypothesis of a two-pathway mechanism:



Here (*a*) is the usual pathway which was already considered above and (*b*) is the pathway involving the formation of a complex between the heteropolyanion and the olefin, in which the latter is activated as a result of the coordination to the heteropolyanion. It has been suggested that the increase in the order of reaction with respect to the heteropolyacid may in fact be explained by the presence of pathway (*b*).

In reality both mechanisms of this industrially important reaction are probably in essence the same and the difference consists merely in the interpretation of the influence of the medium. In one case, this is done within the framework of the traditional approach involving allowance for the salt effect, where the medium is regarded as a continuum, whilst in the other this is done at the molecular level during the formation of weak complexes between the heteropolyanion and the substrate. In our view, further investigations in order to find evidence for the possibility of the formation of such complexes are of great interest.

b. Heterogeneous catalysis

In heterogeneous systems, heteropolyacids also exhibit a very high activity. As a rule, heteropolyacids are more active than traditional catalysts such as Al_2O_3, $Al_2O_3-SiO_2$, the HX and HY zeolites, etc., which is fully consistent with the relative strengths of the solid acids.[2, 4, 6] As already mentioned, heteropolyacids exhibit a purely Brønsted acidity, in contrast to oxide systems which have both Brønsted and Lewis acid centres.

Massive heteropolyacids possess very strong and fairly uniform protic centres, but their specific surface is low (1–5 $m^2\ g^{-1}$). Following deposition on an inert carrier, the accessible surface of the heteropolyacid increases, but the acid centres become weaker and less uniform.[59] For reactions occurring on moderately strong acid centres in the vapour or liquid phase, 20% HPA/SiO_2, where HPA = $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$, while SiO_2 is coarsely porous silica gel with a specific surface of 200–300 $m^2\ g^{-1}$, may serve as the optimum catalyst. Such a catalyst may be obtained by impregnating SiO_2 with an aqueous solution of the heteropolyacid with subsequent drying in air and activation by vacuum heat treatment at 200–250 °C. The heteropolyacid exists on the surface of this catalyst in the form of isolated molecules and 50 Å clusters; the Keggin structure of the heteropolyacid is retained under these conditions.[32]

Massive heteropolyacids behave in many respects like solutions, which provides a basis for the expectation of a similarity in

the mechanisms of the action of homogeneous and heterogeneous heteropolyacid-based catalysts. This is associated primarily with the fact that both in solution and in the solid state heteropolyacids have the same molecular (Keggin) structure. The high proton conductivity of the heteropolyacids and their ability to form solvates with polar organic molecules also play an important role.[2, 4, 6] These properties are manifested more strikingly in low-temperature reactions (< 300 °C), where the Keggin structure is retained.

The strength of solid heteropolyacid hydrates diminishes in the sequence[4]

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

which is identical with the series based on the strength of the heteropolyacids in solutions (Table 2). The catalytic activity of the heteropolyacids usually diminishes in the same sequence in both homogeneous and heterogeneous systems.[2, 4]

The hydrates of heteropolyacids exhibit a high proton conductivity.[2-4, 6] The migration of H^+ via the system of hydrogen bonds constituting the crystal structure of the heteropolyacid takes place with a low activation energy and virtually just as readily as in aqueous solutions, the electrical conductivity increasing with increase in the degree of hydration of the heteropolyacids. The anomalously high mobility of H^+ may be one of the reasons for the high catalytic activity of massive heteropolyacids, since it increases the effective concentration of H^+ in the surface region.

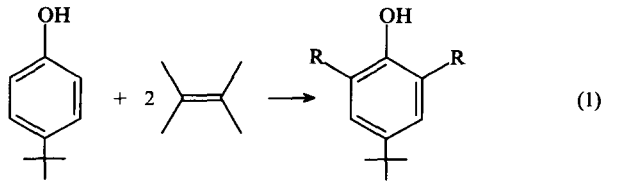
Solid heteropolyacids and their soluble salts have a high affinity for the molecules of polar substances such as alcohols, ketones, ethers, amines, etc. These substances are absorbed in large amounts in the bulk of the crystalline heteropolyacids with formation of solvates.[2-4, 6] The sorption of non-polar hydrocarbons (alkanes, olefins, arenes) is insignificant. They are adsorbed only on the surface of the heteropolyacids.

Because of the ease of sorption of polar molecules, their catalytic reactions can occur not only on the surface but also in the bulk of massive heteropolyacids. Solid heteropolyacids behave in relation to polar substances very similarly to concentrated solution, i.e. all the acid protons, and not only the surface protons, participate in the catalytic reaction. This phenomenon, unusual for heterogeneous acid catalysis, is designated by the term 'pseudoliquid phase'.[2, 6] In contrast to polar molecules, non-polar reagents are incapable of being absorbed in the bulk phase of heteropolyacids; they interact only with the surface of the catalyst. The 'pseudoliquid phase' apparently plays a significant role in reactions of polar substances at low temperatures, i.e. under conditions where the degree of sorption of the substrate in the bulk phase of the catalyst is high. In high-temperature processes, the contribution of the bulk phase reaction is probably not so significant. For a more detailed treatment, see other communications.[2, 4, 6]

4. Alkylation, dealkylation, and transalkylation of phenols

These reactions are of practical importance and are used widely in industry to obtain antioxidants, thermo- and photo-stabilisers, biologically active substances, etc. A wide variety of acid–base catalysts are used to carry them out: inorganic acids, sulfonic acids, cation-exchange resins, aluminosilicates, and metal salts and oxides.[61-64]

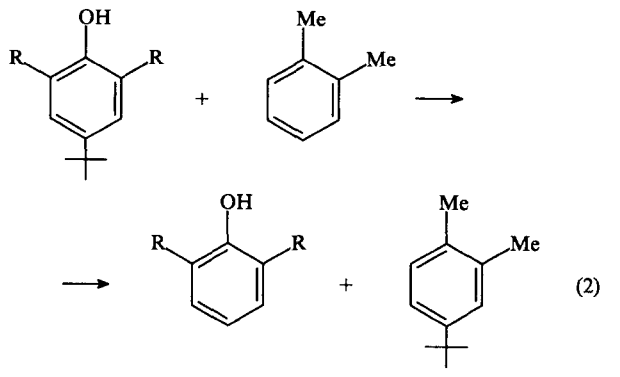
Heteropolyacids exhibit a high catalytic activity in reactions involving the alkylation of benzene and alkylbenzenes by olefins.[34, 65-67] Phenol is also readily alkylated on heteropolyacids, but the reaction in non-selective.[68-71] *p*-(*tert*-Butyl)phenol (TBP) is alkylated more selectively. Its reaction with cyclohexene, hex-1-ene, styrene, and benzyl chloride in the presence of the massive acids $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ and the acids deposited on SiO_2 (1% relative to TBP) at 100–150 °C affords 2,6-dialkyl-4-*tert*-butylphenols in 63%–90% yield.[68, 69]



(1)

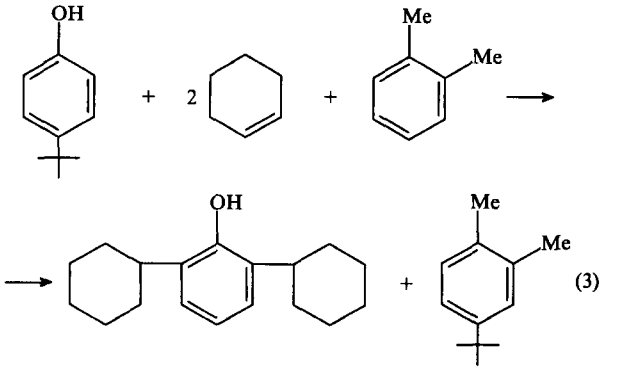
The most selective reaction is that with styrene: the yield reaches 90% for 100% conversion of TBP (100–110 °C, 1 h). In the case of α-methylstyrene, monoalkylation takes place preferentially and the yield of 4-*tert*-butyl-2-cumenylphenol is 70%.

The alkylation of TBP by olefins in the presence of heteropolyacids in *o*-xylene, which is an acceptor of the *tert*-butyl group, makes it possible to obtain 2,6-dialkylphenols without the intermediate isolation of 2,6-dialkyl-4-*tert*-butylphenol. The *tert*-butyl group is eliminated quantitatively via the reaction



(2)

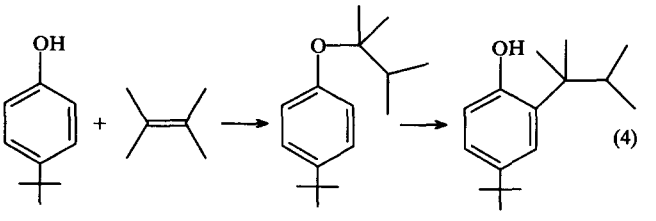
2,6-Dicyclohexylphenol was obtained in this way in 77% yield.[68, 69] The *tert*-butylxylene formed in this reaction can be used in the synthesis of pigments.



(3)

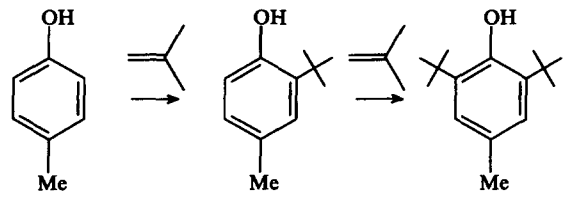
Heteropolyacids are insoluble in the reaction mass, are readily separated from the latter, and can be reused.

The alkylation of TBP apparently proceeds via a mechanism involving the formation of ethers as the primary products with their subsequent rearrangement to the *C*-alkylation products. This has been confirmed by the detection of ethers in the initial stage of the reaction.[68, 69]



(4)

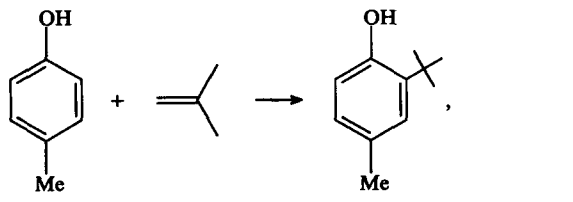
The acid alkylation of *p*-cresol by isobutene is an important industrial reaction used in the synthesis of phenolic antioxidants.[62]



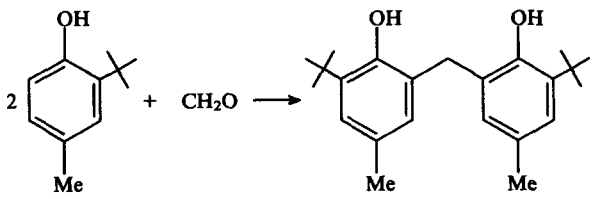
(5)

This reaction proceeds smoothly when the heteropolyacid is used as a heterogeneous catalyst. The activity of heteropolyacids in the *p*-cresol and TBP alkylation reactions (calculated per available proton) is greater by four orders of magnitude than the activity of sulfuric acid, which can be explained by the stronger acidity of the heteropolyacid.[68]

An industrial version of the alkylation of *p*-cresol by isobutene in the presence of $H_3PW_{12}O_{40}$ has been developed at the Institute of Catalysis of the Siberian Division of the Russian Academy of Sciences. This reaction is the first stage of the synthesis of the antioxidant Agidol-2 [2,2'-methylenebis(6-*tert*-butyl-4-methylphenol)], widely used to stabilise polymeric materials.[62]



(6)

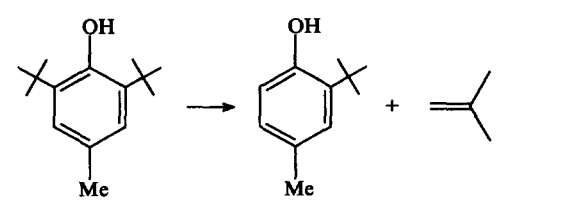


(7)

Agidol-2

The second stage [reaction (7)] is carried out by familiar method with HCl as the catalyst.[62] The use of a heteropolyacid instead of sulfuric acid made it possible to eliminate completely the formation of toxic cresol-sulfate waste water in the first stage of the process. The consumption of *p*-cresol was reduced, because its sulfonation and losses during neutralisation and washing were eliminated. The duration of the alkylation stage was shortened and charring was sharply reduced.

The dealkylation of derivatives of 2,6-di-*tert*-butylphenol to 2-*tert*-butylphenols is also widely used in the synthesis of phenolic antioxidants.

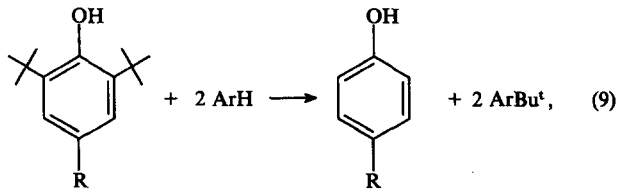


(8)

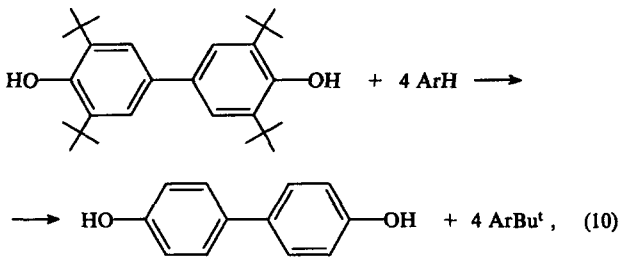
The acids $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ are effective homogeneous and heterogeneous catalysts of this reaction, in which the substituents can be not only the methyl group but also H, Et, and CH_2CH_2COOMe.[72–74] The heterogeneous process takes place at 130–150 °C in the presence of a catalyst (<1%) in the substrate melt.[72, 73] Molybdenum heteropolyacids are rapidly deactivated as a result of their reduction by the reaction medium. Heteropolyacids are tens of times more active than heterogeneous catalysts such as cation-exchange resins, aluminosilicates, aluminium sulfate, etc. The homogeneous process is even more effective. In solution in acetic acid, dealkylation takes place even at 80 °C. The catalytic activity of heteropolyacids is correlated with their strength and exceeds by a factor greater than 100 the activity of sulfuric acid.[74]

The transalkylation of 2,6-di-*tert*-butylphenols in the presence of heteropolyacids has been studied in detail.[70, 75–77] This important reaction is used widely in organic synthesis for the regioselective introduction of functional groups in phenols.[78, 79] Aromatic compounds (ArH) such as benzene, toluene, *o*-xylene, naphthalene, etc. are used as acceptors of the *tert*-butyl group, while the catalysts are H_2SO_4, $4\text{-}MeC_6H_4SO_3H$, $MeSO_3H$, CF_3SO_3H, zeolites, aluminosilicates, and the perfluorosulfonic acid cation exchanger Nafion-H.[78–81]

Massive and deposited tungsten heteropolyacids (0.5–7%) are universal catalysts of the complete *trans*-de-*tert*-butylation of phenols



(9)



(10)

where R = H, Me, Et, $(CH_2)_2COMe$, $(CH_2)_2COOMe$, $(CH_2)_3OCOMe$, $(CH_2)_3Cl$, and $(CH_2)_3OCOC_{17}H_{35}$. These reactions take place at 100–140 °C with the molar ratio ArH : (2,6-di-*tert*-butylphenol) = 2 : 1 in 0.2–4 h with a yield of 92%–98%. The best *tert*-butyl group acceptors are toluene and *o*-xylene. The catalyst can be readily separated from the reaction mass and can be reused. Heteropolyacids are more active in the transalkylation reaction of phenols compared with other acid catalysts. Even Nafion-H, the strength of which is similar to that of superacids,[82] is appreciably inferior to heteropolyacids as regards activity in these reactions.[76, 81]

The de-*tert*-butylation reaction of 2,6-di-*tert*-butylphenols is first-order with respect to phenol and heteropolyacid. Its rate depends on the nature of ArH. This dependence is analogous to that observed in electrophilic substitution in aromatic compounds. The rate constant ratios k_{ArH}/k_{PhH} at 20 °C (2% $H_3PW_{12}O_{40}$) are given below:[77]

ArH	PhH	PhMe	PhBu^t	*o*-$Me_2C_6H_4$	*m*-$Me_2C_6H_4$
k_{ArH}/k_{PhH}	1.0	6.9	1.5	12	0.95

When catalysts on a carrier are used, the rate of reaction depends significantly on the amount of deposited heteropolyacids. Fig. 4 illustrates the dependence of the rate constants k_t and k_s for the de-*tert*-butylation of 2,6-di-*tert*-butyl-4-methylphenol on the amount of the acid $H_3PW_{12}O_{40}$ deposited on silica gel (k_t and k_s are the rate constants referred respectively to the total number of protons of the heteropolyacid in the catalyst and to the number of surface protic centres of the heteropolyacid). With increase in the amount of the deposited heteropolyacid, the strength of the protic

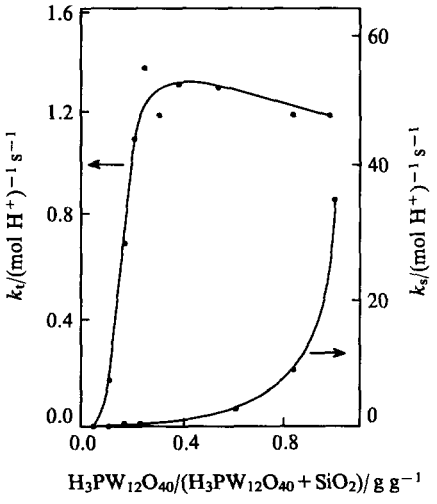
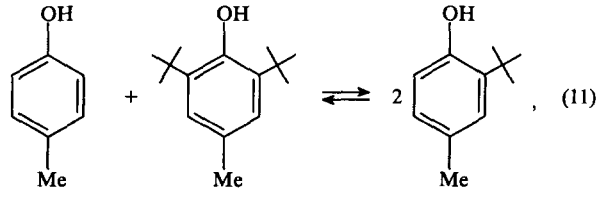


Figure 4. Dependence of the constants k_t and k_s on the ratio $H_3PW_{12}O_{40}/(H_3PW_{12}O_{40} + SiO_2)$.[77]

centres also increases and there is a simultaneous decrease in the surface area of the catalyst and hence a decrease in the number of accessible protic centres. Evidently k_t increases rapidly with increase in the concentration of the heteropolyacid on the carrier, reaches a maximum, and then slowly decreases. This type of dependence has been explained by the competitive influence of the increase in the strength of the acid centres, on the one hand, and the decrease in their number on the catalyst surface, on the other.[77] A similar dependence has been observed in the vapour phase dehydration of *tert*-butyl alcohol on $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$.[83] In contrast to k_t, the constant k_s increases monotonically with increase in the heteropolyacid concentration on the carrier, which indicates the existence of a correlation between the catalytic activity and the strength of the acid centres.[77]

Heteropolyacids are effective catalysts of the reaction



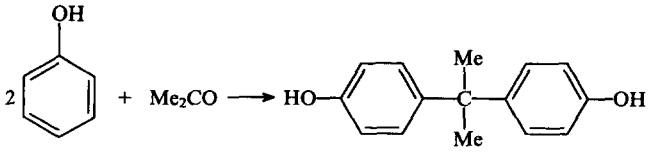
(11)

which, together with reaction (5) and (8), is used in industry for the synthesis of phenolic oxidants. In this case too, heteropolyacids are more active than sulfuric acid by four orders of magnitude per accessible proton.[76]

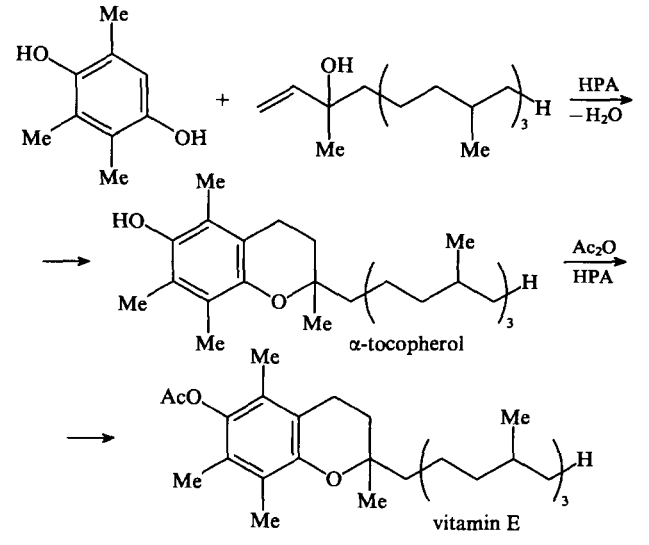
An industrial method of synthesis of 2-*tert*-butyl-4-methylphenol via reaction (11) using heteropolyacids instead of sulfuric acid has been developed at the Institute of Catalysis of the Siberian Division of the Russian Academy of Sciences. It has the same advantages as the alkylation of *p*-cresol via reaction (6) examined above.

5. Condensation reactions

Heteropolyacids have long been used as catalysts of condensation reactions.[4] They catalyse the condensation of acetone with formation of mesityl oxide and alkylbenzenes under both homogeneous[84, 85] and heterogeneous[86] conditions. Bisphenols are obtained by condensing phenols and ketones in the presence of a heteropolyacid:[87]

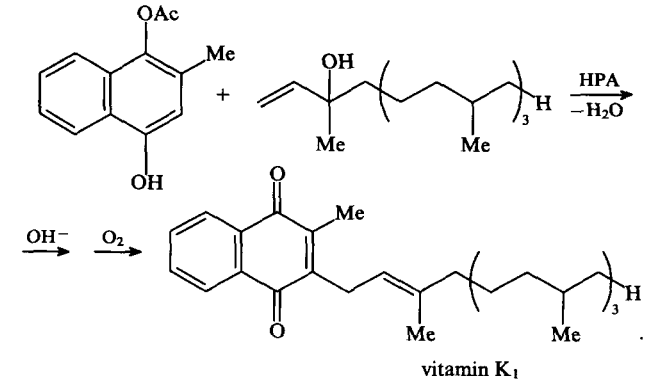


It has been established recently that heteropolyacids catalyse effectively the condensation stage in the synthesis of vitamins E, K_1, and C.[88–90] The acids $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ catalyse the condensation of isophytol with 2,3,5-trimethylhydroquinone (TMHQ) with formation of α-tocopherol and the conversion of the latter into the acetate (vitamin E):[88, 89]

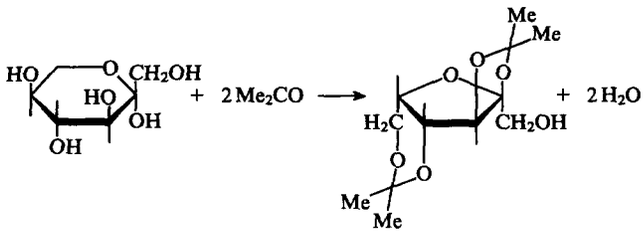


The condensation reaction proceeds both in homogeneous (in acetic acid and butanol) and heterogeneous (in toluene and *o*-xylene) systems. Heteropolyacids are introduced in an amount of about 1% relative to TMHQ. The yield of the product reaches 91%–92% and the content of vitamin E in the latter is 95%. In industry, $ZnCl_2$ or sulfuric acid is used as the catalyst for the synthesis of α-tocopherol.[91] When $ZnCl_2$ is employed, a high-quality product (yield ~80%) is obtained with a vitamin E content in excess of 95%.[92] A significant disadvantage of this method is the high consumption of the catalyst (about 1 mol of $ZnCl_2$ per mole of TMHQ) and the formation of a large amount of waste. When sulfuric acid is used, the product contains 10–20% of impurities which are difficult to separate from vitamin E.[93] The use of heteropolyacids instead of $ZnCl_2$ increases the yield of vitamin E by 10% without reducing the quality of the product. Heteropolyacids can be readily separated from the reaction mass without neutralisation and can be reused.

Heteropolyacids are also effective in the related condensation reaction between isophytol and 1-acetoxy-4-hydroxy-2-methylnaphthalene, which is a key stage in the synthesis of vitamin K_1.[88, 89] In this reaction, heteropolyacids are approximately 50 times more active than $ZnCl_2$ and aluminosilicates.[94]

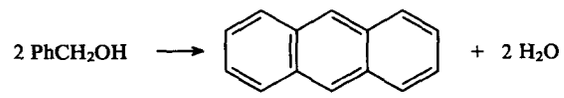


The reaction of L-sorbose with acetone — one of the stages in the synthesis of L-ascorbic acid (vitamin C) — takes place in acetone and the yield of diacetone-L-sorbase (DAS) in the presence of 0.1%–0.35% of $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$ as the catalyst is then 85%.[88, 90]



The water formed in the reaction is distilled away or eliminated by absorbing it with the NaA zeolite. The reaction of L-sorbose with acetone is carried out in industry in the presence of oleum (the yield of DAS is ~80%[91]). Oleum is added in a large amount (~5% relative to acetone), because it serves both as the catalyst and as the dehydrating agent. A disadvantage of this process is the large amount of sodium sulfate waste obtained when oleum is neutralised. Thus the use of heteropolyacids makes it possible to increase appreciably the yield of DAS and to diminish significantly the amount of waste on neutralisation of the catalyst.

Heteropolyacids catalyse the condensation of benzyl alcohol with formation of anthracene, but the yield of anthracene is lower than in the case where weaker solid acids, such as the HY zeolite and fluorinated alumina, are used.



In terms of the yield of product at 300 °C, the catalysts can be arranged in the following sequence (the yield expressed as a percentage is indicated in brackets): Al_2O_3 (14) < $H_4SiW_{12}O_{40}$ (25) < $H_3PW_{12}O_{40}$ (33) < F^-/Al_2O_3 (46) < HY (50). The reason for the lower activity of the heteropolyacids may be their small specific surface compared with HY and F^-/Al_2O_3 and also the absence of Lewis acid centres from the heteropolyacid if such centres are required for the given reaction.[95]

The polycondensation of benzyl alcohol is catalysed by $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$.[96] The chiral acid $H_6P_2Mo_{18}O_{62}$, having the Dawson structure, induces the asymmetric polycondensation of benzyl alcohol.[97] In the presence of the homogeneous *l*-brucine–$H_6P_2Mo_{18}O_{62}$ system, benzyl alcohol is converted into an optically active polybenzyl:

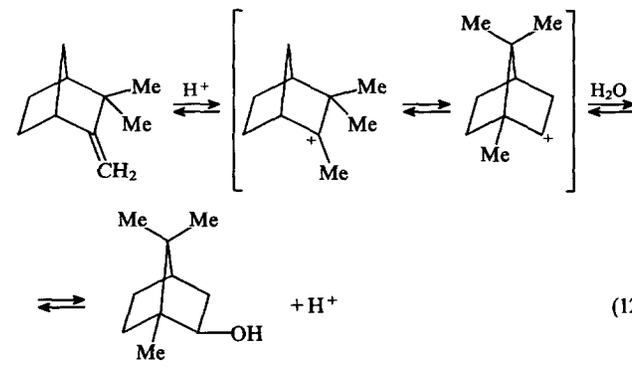
$$n\mathrm{PhCH_2OH} \longrightarrow \{\mathrm{C_6H_4CH_2}\}_n + (n-1)\mathrm{H_2O}\ .$$

When the non-chiral acid $H_6P_2Mo_{18}O_{62}$ is used, an optically inactive polybenzyl is produced.

6. Hydration reactions

The hydration of olefins in the presence of heteropolyacids has been thoroughly investigated in both liquid and vapour phases.[4] As already mentioned, the liquid-phase hydration of propene and butenes in the presence of heteropolyacids is used in industry to synthesise the corresponding alcohols.[7]

The acids $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ proved to be excellent catalysts of the homogeneous hydration of camphene to isoborneol — an intermediate in the synthesis of camphor (50 °C, [HPA] = 0.05 in a Me_2CO–H_2O mixture):[98]



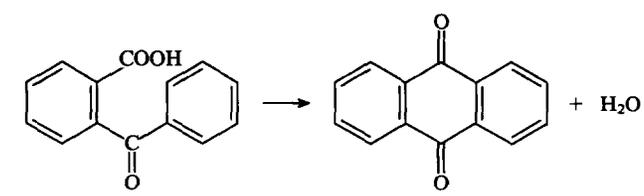
(12)

Isoborneol is virtually the only product of this reaction. The degree of conversion of camphene is 35%. The stronger acid $H_3PW_{12}O_{40}$ is somewhat more active than $H_4SiW_{12}O_{40}$. In the presence of sulfuric acid, reaction (12) proceeds much more slowly: under comparable conditions, the degree of conversion of camphene does not exceed 3%. This reaction may be of practical interest as a direct single-stage method of synthesis of isoborneol. The existing method of its synthesis consists of two stages and bornyl acetate is formed as an intermediate.

When cycloalkenes are hydrated in the presence of a catalyst consisting of a concentrated aqueous solution of an aromatic sulfonic acid and a tungsten heteropolyacid with the Keggin structure, cycloalkanols are formed with a selectivity >99%. The use of heteropolyacids makes it possible to increase the yield of the alcohols and to lower the corrosion activity of the reaction mixture.[99]

The hydration of phenylacetylene in the presence of a heteropolyacid at 60 °C has been investigated. Heteropolyacids are more active in this reaction than sulfuric or perchloric acid.[100]

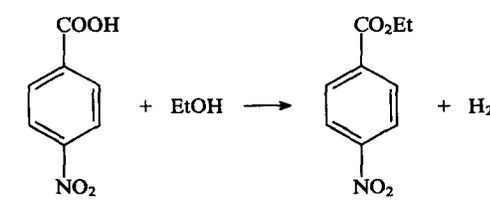
The heteropolyacid $H_3PW_{12}O_{40}$ can be used instead of sulfuric acid as the catalyst of the dehydration of *o*-benzoylbenzoic acid to anthraquinone.[101]



7. Esterification (etherification) reactions

Heteropolyacids are effective catalysts of the synthesis of ethers and esters.[4] Their use in esterification reactions in the synthesis of medicinal preparations is promising.

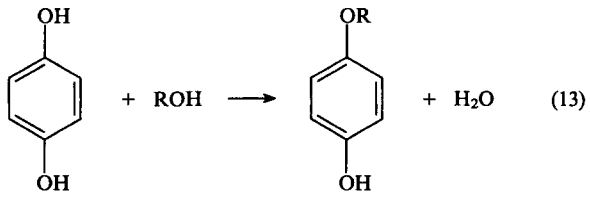
The ethyl ester of *p*-nitrobenzoic acid (PNBA) — an intermediate in the synthesis of the analgesic preparations anesthesin and novocain — was obtained in a yield >99% by esterifying PNBA with ethanol in the presence of $H_3PW_{12}O_{40}$ (3%–7%) at 75 °C.[102]



The water formed in the reaction is distilled away as the azeotrope with toluene. At the end of the reaction, the reaction mass divides into two separate phases. The upper layer contains ethyl *p*-nitrobenzoate mixed with toluene and the alcohol and the lower consists of a solution of the heteropolyacid in ethanol. As a result of this, the catalyst can be readily separated from the reaction product without neutralisation and can be reused. Activity is not lost under these conditions.

Sulfuric acid is used industrially as the catalyst for the synthesis of the ethyl ester of PNBA. This method is characterised by a low yield of the product (75%) and a large amount of waste formed as a result of the neutralisation of sulfuric acid.[103] Thus the application of heteropolyacids in this reaction makes it possible to increase significantly the yield of the product and to diminish the amount of waste. The catalytic activity of the heteropolyacids in the esterification of PNBA is close to that of the KU-2-8 cation-exchange resin[104]

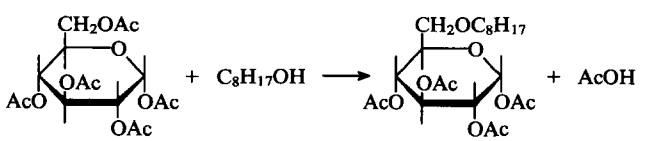
Massive heteropolyacids and heteropolyacids deposited on SiO_2, Al_2O_3, or TiO_2 are used as catalysts of the synthesis of hydroquinone monoethers, which are employed in the manufacture of medicinal preparations and perfumes, stabilisers, polymerisation inhibitors, etc. For example, the use of 1-hexanol in reaction (13) makes it possible to obtain the corresponding monoether with a selectivity of 99% in the presence of $H_3PMo_{12}O_{40}$ (3%) for a hydroquinone conversion of 83% (105 °C, 5 h).[105]



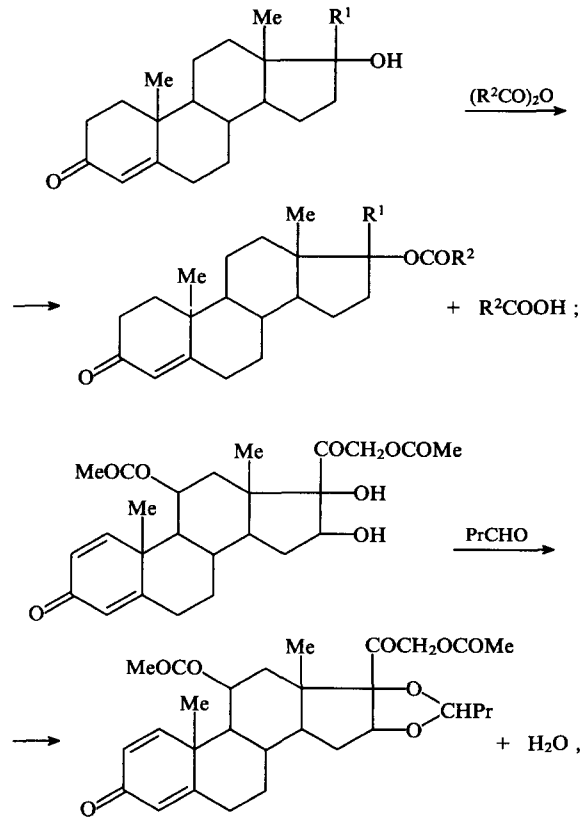
(13)

Dialkyl phthalates, which are used as plasticisers, have been obtained by esterifying phthalic anhydride with C_8-C_{10} alcohols at 100–120 °C in the presence of the homogeneous or heterogeneous $H_3PW_{12}O_{40}$ catalyst (1%–2%). In the latter case, the heteropolyacid deposited on activated charcoal was employed. The catalytic activity of the heteropolyacid is greatly superior to that of H_2SO_4 and toluene-*p*-sulfonic acid. The HPA/C catalyst is less active than the homogeneous catalyst, but has the advantage of being readily removed from the reaction mixture.[106]

The synthesis of glycosides using heteropolyacids as catalysts is of industrial importance.[7] There exist numerous patents concerning the use of this reaction. On interaction with alcohols in the presence of a heteropolyacid (85 °C, 4 h), monosaccharides are readily converted into glycosides in 47%–83% yield. Thus the reaction of pentaacetylglucose with 1-octanol in the presence of $H_3PMo_{12}O_{40}$ (3%) afforded octyl tetraacetylglucoside in 70% yield.[107] Glycosides have found applications as medicinal preparations.



The esterification of steroids and their conversion into acetals take place with quantitative yields in the presence of the catalysts $H_3PW_{12}O_{40}$ and 25% $H_3PW_{12}O_{40}/SiO_2$ (1.5%–9%) in MeCN, CH_2Cl_2, or C_6H_6 (40–82 °C, 0.5–4 h):



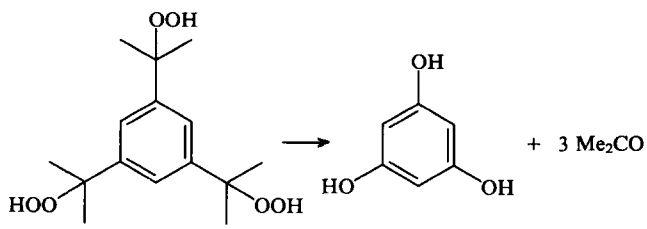
where R^1 = H or COMe and R_2 = Et or Pe.[108] These reactions represent stages in the synthesis of modified hormones.[109] In benzene, where the heteropolyacid is insoluble, such reactions proceed heterogeneously; the catalyst can be separated from the reaction mixture without neutralisation and can be reused. The activity of the heteropolyacid is close to that of $HClO_4$ and is much greater than that of 5-sulfosalicylic acid.

8. Other reactions

The acids $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ catalyse the acylation of aromatic compounds (the Friedel–Crafts reaction).[110–112]

Heteropolyacids are highly active and selective homogeneous[36, 113] and heterogeneous[114, 115] catalysts for the decomposition of cumenyl hydroperoxide to phenyl and acetone. Phloroglucinol was obtained by means of a similar procedure involving the decomposition of 1,3,5-tris(hydroperoxy-isopropyl)benzene in the presence of a heteropolyacid at 50–100 °C with a selectivity of 97% and a hydroperoxide conversion of 89%.[116]

The hydrolysis of sucrose in the presence of $H_4SiW_{12}O_{40}$ has been investigated.[117]



III. Liquid-phase oxidation reactions

The liquid-phase oxidation of organic substances catalysed by heteropolyanions takes place in homogeneous or heterogeneous (two-phase) systems. In the latter case, phase transfer catalysts are frequently used. O_2, H_2O_2, alkyl hydroperoxides and, more rarely, other substances are used as oxidants. The oxidation-reduction properties of heteropolyacids, their synthesis, state in the solution, and applications as catalysts of liquid-phase oxidation have been examined in a number of reviews.[2, 3, 8, 13, 118-120]

1. Oxidation with oxygen

Mixed molybdovanadophosphoric heteropolyanions $PMo_{12-n}^{6+}V_n^{5+}O_{40}^{(3+n)-}$ (HPAN-n, n = 2–6) are used preferentially as catalysts in these reactions.[3, 8, 118-120] They have a fairly high oxidation potential [0.7 V relative to the normal hydrogen electrode (n.h.e.)] and are themselves capable of oxidising a large number of organic and inorganic substances. At the same time, the HPAN-n are reversibly acting oxidants, i.e. their reduced forms can be readily reoxidised to the initial HPAN-n with the aid of O_2.

$$\text{Red} + \text{HPA-}n + i\,H^+ \longrightarrow \text{Ox} + H_iHPA\text{-}n\,, \quad (14)$$

$$H_iHPA\text{-}n + i/4\,O_2 \longrightarrow \text{HPA-}n + i/2\,H_2O\,. \quad (15)$$

Here Red and Ox are respectively the i-electron reductant (substrate or the reduced form of the cocatalyst) and its oxidised form, $H_iHPA\text{-}n = H_i[H_{3+n}PMo_{12-n}^{6+}V_{n-i}^{5+}V_i^{4+}O_{40}]$ is a heteropolyblue, i.e. the reduced form of HPAN-n ($i \leqslant n$).[3, 8, 118-120] The reversibility of the oxidation-reduction reactions of HPAN-n in fact constitutes the basis of their use as catalysts of a large number of liquid-phase oxidation reactions. Certain other mixed heteropolyanions, having similar properties, for example, $H_3PMo_6W_6O_{40}$, are also used for this purpose.[121, 122]

The HPAN-n-catalysed oxidation reactions proceed via a multistage mechanism in conformity with Eqns. (14) and (15).[3] Reactions (14) and (15) can be carried out simultaneously in one reactor or separately. In the second case, direct contact between the organic substrate and O_2 is excluded. The catalysts may be the HPAN-n themselves (one-component systems) or their combinations with other compounds (two-component systems). Among the latter, the HPAN-n + Pd(II)/Pd(0) redox system is the most important. It is analogous to the catalytic system $CuCl_2$ + Pd(II)/Pd(0) used to oxidise ethylene to acetaldehyde (the Wacker process), but, in contrast to the latter, it can work in the absence of Cl^- ions, which increases the selectivity of the process and lowers the corrosion activity of the catalyst solution.[3] The use of the HPAN-n + Pd(II) system in liquid-phase oxidation reactions has been examined in a number of studies.[3, 8, 118-120] Other redox systems based on HPAN-n are also known. Their second component is Tl(III)/Tl(I),[123, 124] Pt(IV)/Pt(II),[125] Ru(IV)/Ru(III), Ir(IV)/Ir(III),[126] Br_2/Br^-,[127] and I_2/I^-.[128] In two-component systems, the substrate is usually oxidised by the cocatalyst and the HPAN-n ensures the regeneration of the cocatalyst via reactions (14) and (15).

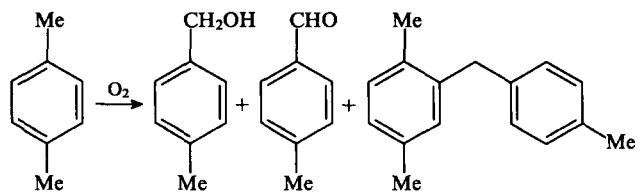
The HPAN + Pd(II) and HPAN + Rh(I) systems are also used in carbonylation hydroformylation, and hydrogenation reactions.[129-133]

Homogeneous catalysts based on HPAN-n consist as a rule of complex equilibrium mixtures of polyanions of different composition with products of the degradative dissociation of the heteropolyanion. All these species can function as the active form of the catalyst. Thus, in oxidation of hydrogen sulfide by the Mo_{12}-molybdophosphate at pH 3, the active role is played by isopolyanions for example, $Mo_7O_{24}^{6-}$ or $Mo_8O_{26}^{4-}$ in equilibrium with the heteropolyanion.[134] In the oxidation of alkylbenzenes and phenols by oxygen in the presence of HPAN-n, the true oxidant is most likely to be the VO_2^+ ions formed as the result of the dissociation of HPAN-n.[135-137]

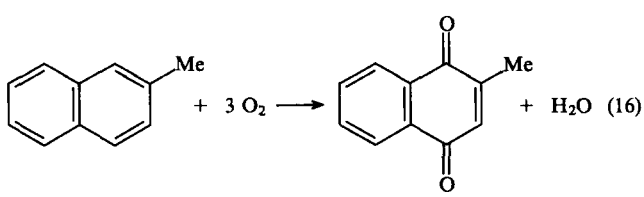
Free vanadium(IV) in the form of the VO^{2+} ion is hardly oxidised in acid aqueous solutions but is fairly readily oxidised when it is part of the compositions of HPAN-n [Eqn. (15)].[3] This reaction proceeds via a many-electron mechanism involving the consecutive transfer of three or four electrons in the complex of H_iHPA-n with O_2.[3] In contrast to the HPAN-n blues, the more readily oxidised blues derived from the tungsten heteropolyanions $PW_{12}O_{40}^{3-}$ and $SiW_{12}O_{40}^{4-}$ (E = 0–0.1 V) are oxidised by O_2 via a one-electron mechanism.[138]

a. Oxidation of arenes

Heteropolyanions in acetic acis solutions oxidise methylbenzenes with formation of a mixture of aromatic alcohols, aldehydes, and di- and poly-aryl methanes. In the presence of O_2, the reaction can proceed catalytically.[135] The true arene oxidants are probably the VO_2^+ ions which have emerged from the coordination sphere of HPAN-n. The rate of oxidation of arenes decreases in the sequence durene > mesitylene > p-xylene > toluene. The reaction apparently proceeds via the formation of aromatic radical-cations as intermediates.[135]



2-Methylnaphthalene (MN) is oxidised to 2-methyl-1,4-naphthoquinone by oxygen (3–8 atm) in the presence of 0.02–0.2 M HPAN-n as the catalyst. The reaction is carried out in a $AcOH-H_2O-H_2SO_4$ solution at 120–140 °C and its selectivity is 82% for a 2-methylnaphthalene conversion of 78%.[139] 2-Methyl-1,4-naphthoquinone is an intermediate in the synthesis of group K vitamins. It is obtained industrially by the stoichiometric oxidation of 2-methylnaphthalene by chromium trioxide in 40–50% yield.[91, 140] This reaction can be carried out catalytically with a higher yield with the aid of HPAN-n an O_2 as the oxidant:



Heteropolyanions catalyse the oxidative ring bromination of arenes with HBr as the brominating agent and O_2 as the oxidant.[127]

$$ArH + HBr + \frac{1}{2}O_2 \longrightarrow ArBr + H_2O\,.$$

The arenes brominated include benzene, its derivatives, naphthalene, thiophene, etc. The reaction proceeds in an $AcOH-H_2O-H_2SO_4$ solution at 50–100 °C. The bromination of the ring in arenes is effected by Br_2, which is formed as a result of the bromination of bromide ions by HPAN-n. In the case of alkylbenzenes, the alkyl groups are also oxidised. An advantage of this method is the possibility of using Br^- in the reaction instead of Br_2.

The HPAN-n + HBr system brominates phenol selectively in the *para*-position.[141]

Many stoichiometric reactions involving the oxidation of organic substances by palladium(II) compounds can be carried out catalytically with O_2 as the oxidant and the HPAN-n + Pd(II) two-component system as the catalyst.[3, 8, 118-120] Thus the

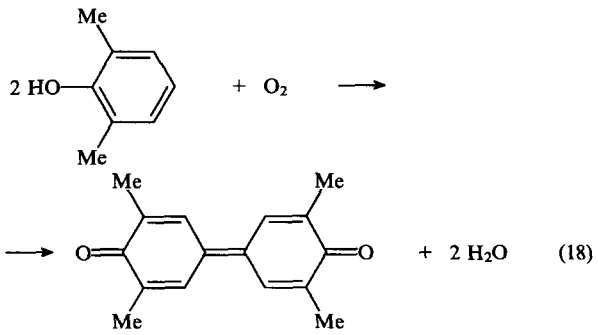
oxidative coupling of arenes in the presence of the HPAN-*n* + Pd(II) system makes it possible to obtain in a single stage biaryls — valuable intermediates in inorganic synthesis:

$$2\,ArH + \frac{1}{2}O_2 \longrightarrow Ar-Ar + H_2O, \quad (17)$$

where ArH = C_6H_6, PhAlk, PhCl, PhCOOH, $PhCF_3$, thiophene, etc.[142-144] The reaction proceeds under very mild conditions at 50–90 °C and an O_2 pressure of 1.5 atm. The selectivity in relation to biaryls is 70%–93%. It is noteworthy that in the absence of HPAN-*n*, reaction (17) requires a temperature of 150 °C and a pressure of 25 atm.[120] The mechanism of the oxidative coupling of arenes under the influence of palladium(II) has been examined in other reviews.[120, 145]

b. Oxidation of phenols

The compounds of many metals are capable of catalysing the oxidative coupling of phenols to diphenoquinones in solutions.[146] The coupling of 2,6-dialkylphenols (mainly 2,6-xylenol) under the influence of oxygen in the presence of copper complexes of amines is of practical importance:

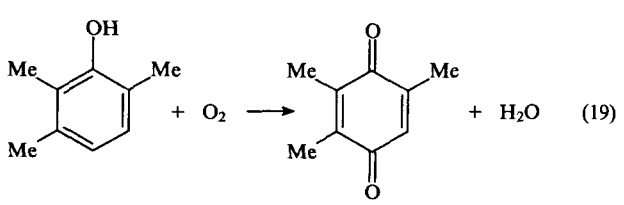


(18)

Diphenoquinones are used to synthesise bisphenols, which are used widely as stabilisers of polymers, oils, etc.[62]

The activity of heteropolyanions in reaction (18) is greater than that of copper compounds. The oxidative coupling takes place in H_2O, AcOH–H_2O, or MeOH–H_2O at 25–50 °C and an O_2 pressure of 1–5 atm. The diphenoquinones are insoluble under these conditions and can be readily isolated from the reaction mixture by crystallisation. The catalyst can be used repeatedly without loss of its activity. 2,2',6,6'-Tetramethyl- and 2,2',6,6'-tetra-*tert*-butyl-diphenoquinones have been obtained by this method in 100% yield relative to the initial phenol.[147]

The oxidation of 2,3,6-trimethylphenol (TMP) is of interest for the synthesis of 2,3,5-trimethyl-1,4-benzoquinone (TMBQ), which is an intermediate in the synthesis of vitamin E.[148] The oxidation of TMP by oxygen in the presence of HPAN-*n* as the catalyst in solution in aqueous acetic acid makes it possible to obtain TMBQ with a selectivity of 86% for 100% conversion of TMP.[136, 137]



(19)

2,2',3,3',6,6'-Hexamethyl-4,4'-bisphenol (HMBP), the product of the oxidative coupling of TMP, is also formed under these conditions. The process selectivity depends on the water concentration in the reaction mixture: with increase in [H_2O], the yield of HMBP increases owing to the decrease in the yield of TMBQ. The bisphenol HMBP itself undergoes oxidative conversion into TMBQ via the intermediate formation of hexamethyldiphenoquinone (HMDQ).

Evidence has been obtained that the activity of the oxidant arises through the VO_2^+ ions formed as a result of the dissociation of HPAN-*n*. A mechanism has been proposed for reaction (19) involving the one-electron oxidation of TMP (ArOH) by VO_2^+ ions with formation of TMBQ and vanadium(IV) followed by the oxidation of vanadium(IV) to vanadium(V) by oxygen in the coordination sphere of HPAN-*n*.[137]

$$\text{HPAN-}n \rightleftharpoons V(V) + \text{HPAN-}(n-1), \quad (20)$$

$$V(V) + ArOH \longrightarrow ArO^{\cdot} + V(IV) + H^+, \quad (21)$$

$$2\,ArO^{\cdot} \longrightarrow HMBD \xrightarrow{Ox} HMDQ \xrightarrow{Ox} TMBQ, \quad (22)$$

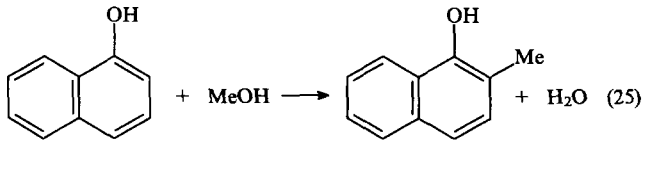
$$V(IV) + \text{HPAN-}n + H^+ \rightleftharpoons V(V) + H(\text{HPAN-}n), \quad (23)$$

$$4\,H(\text{HPAN-}n) + O_2 \longrightarrow 4\,\text{HPAN-}n + 2\,H_2O. \quad (24)$$

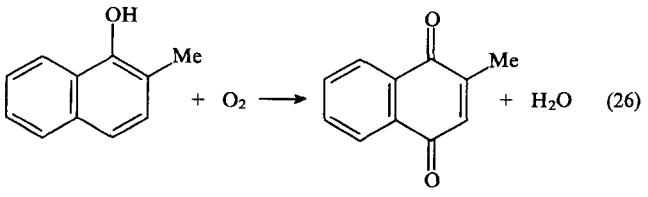
The stage involving the formation of the phenoxyl radical [reaction (21)] is probably rate-limiting.

The oxidation of sterically hindered phenols to benzoquinones by oxygen in the presence of manganese(II) complexes of heteropolytungstates has been investigated.[149]

A new two-stage method of synthesis of vitamin K_3 from 1-naphthol has been developed.[150] It involves the alkylation of 1-naphthol by methanol to 2-methyl-1-naphthol and the oxidation of the latter to 2-methyl-1,4-naphthoquinone.



(25)



(26)

The alkylation reaction (25) is carried out in the vapour phase in the presence of an iron–vanadium catalyst. The oxidation stage (26) is carried out in the liquid phase using HPAN-*n* as the catalyst. Reaction (25) proceeds with a selectivity in excess of 90% and reaction (26) with a selectivity of 83%. As a result of this, the ultimate selectivity greatly exceeds the selectivity in the industrial single-stage synthesis of vitamin K_3 by the stoichiometric oxidation of 2-methylnaphthalene by CrO_3.[91, 140]

2. Oxidation by hydrogen peroxide

The tungsten(VI) and molybdenum(VI) heteropolyanions catalyse various reactions involving the oxidation of organic substances by hydrogen peroxide in homogeneous or two-phase systems under the conditions of phase transfer catalysis. Such reactions include the epoxidation of olefins, the oxidation of alcohols, glycols, phenols, etc.[2] The active intermediates in these reactions are peroxoheteropolycomplexes. In many cases, it was possible to detect them spectroscopically[151, 152] and sometimes to isolate them.[153]

In the homogeneous oxidation of allyl alcohol by H_2O_2 in aqueous solution in the presence of $H_3PW_{12}O_{40}$ at pH 0.7–1.8, glycerol is formed in 64%–100% yield relative to the peroxide which has reacted (70–90 °C, 1–2 h). The primary product is probably an epoxide, which rapidly hydrolyses to glycerol in an acid medium. The peroxo-complexes of heteropolyacids containing up to four peroxo-groups linked to the $PW_{12}O_{40}^{3-}$

anion, have been detected in the reaction system by ^{31}P NMR. The heteropolyacid does not decompose during the reaction.[151]

The catalytic activity of heteropolyanions of different types in the homogeneous reaction involving the oxidation of cyclohexene by hydrogen peroxide in acetonitrile at 35 °C has been investigated. The heteropolyanions employed include $PW_{12}O_{40}^{3-}$ and the lacunary anion $PW_{11}O_{39}^{7-}$ and complexes with transition metal ions $PW_{11}O_{39}M^{x-}$, where M = Ni(II), Co(II), Cu(II), Fe(II), Cr(III), Ru(IV), Ti(IV), and V(V). The anion $PW_{11}O_{39}^{7-}$ shows the highest catalytic activity and selectivity in relation to epoxycyclohexane. The anion $PW_{12}O_{40}^{3-}$ is much less active. The cobalt (II), copper(II), and ruthenium(IV) complexes are inactive in the oxidation of cyclohexene but rapidly decompose H_2O_2. The nickel(II), titanium(IV), and vanadium(V) complexes are inert both in the oxidation of the substrate and in the decomposition of H_2O_2. The iron(II) and chromium(III) complexes are moderately active catalysts of the oxidation of cyclohexene, but the reaction proceeds nonselectively.[152]

Cyclopentene is oxidised by hydrogen peroxide to glutaraldehyde in the presence of the mixed heteropolyacids $H_3PMo_{12-n}W_nO_{40}$ (n = 1–9) in solution in tributyl phosphate (TBP) in 60% yield relative to the H_2O_2 employed (35 °C, 3 h). Water is removed from the H_2O_2–TBP system by vacuum distillation. Other heteropolyacids have been investigated in this reaction. The yield of glutaraldehyde (mol%) decreases in the sequence[154] $H_3PMo_{10}W_2O_{40}$ (16) > $H_3PMo_{12}O_{40}$ (47) > $H_4GeMo_{12}O_{40}$ (21) > $H_3PMo_{10}V_2O_{40}$ (6) > $H_3PW_{12}O_{40}$ (5) > $H_4SiMo_{12}O_{40}$ (1).

The two-phase system including immiscible aqueous and organic phases and a phase transfer catalyst is used widely in reactions involving oxidation by H_2O_2.[154–160] Convenient organic solvents are $1,2\text{-}Cl_2C_2H_4$, $CHCl_3$, CCl_4, C_6H_6, etc. The phase transfer catalysts employed are tetraalkylammonium (C_6–C_{18}) cetylpyridinium, etc. cations (Q^+). The catalytic system is usually prepared as follows. Active peroxo-complexes are formed initially in the aqueous phase from the tungsten(VI) or molybdenum(VI) starting compounds (for example, the heteropolyanions or $WO_4^{2+} + PO_4^{3-}$, etc.) and hydrogen peroxide. The initial heteropolyanions can then partly decompose on reaction with the excess H_2O_2.[161] Next the organic phase with the phase transfer catalyst dissolved in it is added. This results in the formation of Q^+ salts with peroxoheteropolyanions, which are soluble in the organic phase and are almost fully transferred to the latter. This is followed by the addition of the organic substrate, for example, an olefin, and the reaction begins. The oxidation takes place preferentially in the organic phase via the transfer of an oxygen atom from the peroxo-complex to the substrate. The peroxo-complexes are regenerated at the interface via the interaction of the heteropolyanion with the hydrogen peroxide in the aqueous phase. The mechanism of the catalytic epoxidation of the olefins by hydrogen peroxide in the two-phase system in the presence of $PW_{12}O_{40}^{3-}$ is illustrated schematically in Fig. 5.

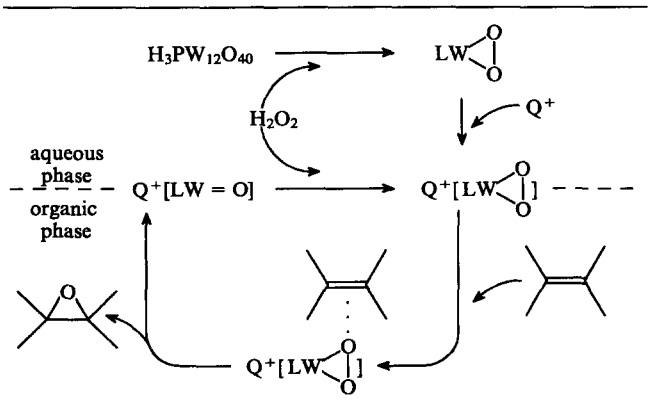


Figure 5. Epoxidation of olefins by hydrogen peroxide in a two-phase system.

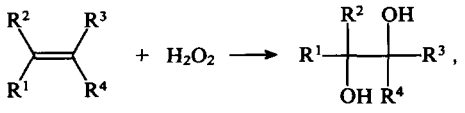
Tetrahexylammonium heteropoly-11-tungstates are active catalysts of the oxidation of cyclohexene by 30% aqueous H_2O_2 in the 1,2-dichloroethane–water two-phase system. The reaction proceeds in the organic phase and the main product is cyclohexanediol. The products of the oxidative cleavage of the ring—adipaldehyde and adipic acid—are also formed in 30%–45% yield. In contrast to the lacunary M_{11}-HPA, the saturated M_{12}-HPA proved to be virtually inactive.[156]

The tetrakis(diperoxotungsto)phosphate $Q_3^+[PW_4O_{24}]^{3-}$ [$Q^+ = N(C_6H_{13})_4^+$, $N(C_8H_{17})_3(CH_3)^+$, etc.] is an effective stoichiometric reagent for the epoxidation of olefins in aprotic solvents and is also an effective catalyst of this reaction with H_2O_2 in a two-phase system.[153, 158] This compound has been isolated and its structure has been characterised by X-ray diffraction[153] (Fig. 6).

The anion $PW_4O_{24}^{3-}$ has the C_2 symmetry and consists of a central PO_4 tetrahedron and four distorted $W(O_2)_2O_3$ pentagonal bipyramids linked to it via the oxygen atoms. The bipyramids are grouped into two pairs with common edges. Each tungsten atom is linked to two peroxide groups located in the equatorial plane of the pentagonal bipyramid. It is of interest to note that tungsten(VI) and molybdenum(VI) have the same coordination environment in their monomeric diperoxo-complexes, which are capable of the effective epoxidation of olefins.[159]

The epoxidation of oct-1-ene with 15% H_2O_2 in the presence of $PW_4O_{24}^{3-}$ in the 1,2-dichloroethane–water system affords epoxyoctane in 89% yield relative to the initial hydrogen peroxide for a H_2O_2 conversion of about 100% (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 is converted into the *trans*-epoxide.[153]

The heteropolyanion in $Q_3^+[PW_4O_{24}]^{3-}$ catalyses the conversion in the two-phase system of water-insoluble olefins of different structure into 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)[158]



where R^1–R^4 = H, Me, Et, Bu, Ph, etc. The glycols formed are present almost entirely in the aqueous phase and can be readily isolated from the reaction mixture. The vicinal glycols are used for the preparation of cosmetics and perfumes, photographic materials, etc.

The epoxidation of oct-1-ene by hydrogen peroxide in the $CHCl_3$–H_2O system has been investigated under the conditions of phase transfer catalysis in the presence of the heteropolyanion $XM_{12}O_{40}^{n-}$ and $X_2M_{18}O_{62}^{n-}$ and the isopolyanions $M_xO_y^{z-}$ (M = Mo or W; X = P, Si, or B) as precursors of catalytically active peroxo-complexes. The state of the complexes in the system has been characterised by a number of spectroscopic methods.

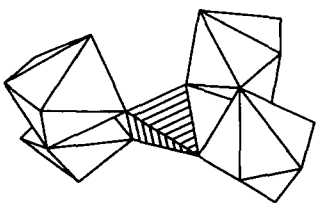


Figure 6. The structure of the peroxoheteropolyanion $PW_4O_{24}^{3-}$ (according to the data of Venturello et al.[153]).

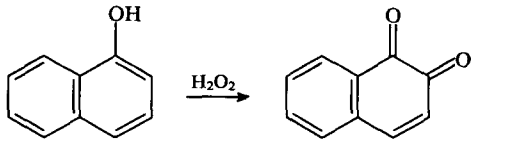
It was established that the anions $BW_{12}O_{40}^{5-}$, $SiW_{12}O_{40}^{4-}$, and $P_2W_{18}O_{62}^{6-}$ are altogether inactive and do not change during the reaction, while $PMo_{12}O_{40}^{3-}$ exhibits a low activity. On the other hand, $PW_{12}O_{40}^{3-}$ exhibits a high activity (the yield of the epoxide is 79% relative to oct-1-ene for a 95% selectivity) when the catalytic system is formed beforehand by the reaction of the heteropolyanion with H_2O_2 in aqueous solution in the absence of Q^+ and oct-1-ene. When all the reagents are mixed simultaneously, the activity of $PW_{12}O_{40}^{3-}$ is zero. A higher activity is shown by tunstic acid (yield 76%) and $H_2W_{12}O_{42}^{10-}$ (yield 67%), their activity being independent of the method used to carry out the reaction. Heteropolyanions having the Keggin structure decompose in the presence of an excess of H_2O_2 {$[H_2O_2]/[M]$ = 30–355 mol mol^{-1}} with formation of the peroxo-complexes $PM_4O_{24}^{3-}$ and $M_2O_{11}(H_2O)_2^{2-}$. It has been suggested that $PM_4O_{24}^{3-}$ is in fact the active species responsible for epoxidation when $PM_{12}O_{40}^{3-}$ is used under the conditions of phase transfer catalysis.[161]

The epoxidation of styrene–butadiene and isobutene–isoprene copolymers by hydrogen peroxide in the presence of $PW_4O_{24}^{3-}$ has been investigated.[162]

The cetylpyridinium salt of $PW_{12}O_{40}^{3-}$, which can be readily obtained by the reaction of $H_3PW_{12}O_{40}$ with three equivalents of cetylpyridinium chloride, catalyses a large number of reactions involving oxidation by hydrogen peroxide. They include the epoxidation of olefins, allyl alcohols, and α,β-unsaturated carboxylic acids, the oxidation of secondary alcohols to ketones, the oxidation of α,ω-diols to lactones, the oxidative cleavage of vicinal diols and olefins to give carboxylic acids, etc. These reactions proceed under mild conditions and with satisfactory yields.[157, 163, 164] Alkynes are also oxidised smoothly in this system to carboxylic acids.[165]

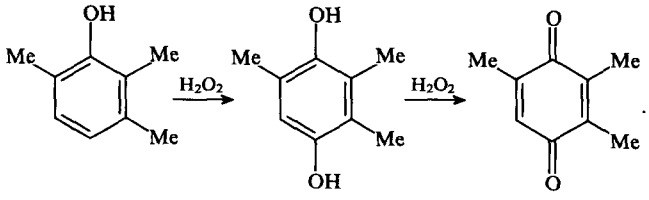
The oxidation of primary and secondary aliphatic and aromatic amines with 35% H_2O_2, catalysed by peroxo-heteropolytungstates, leads to the formation of oximes and nitro-compounds in a high yield in homogeneous or two-phase systems.[166]

α- and β-Naphthols ($\sim 10^{-3}$ M) are oxidised by H_2O_2 (2%–15%) to 1,2-naphthoquinone in 80%–98% yield at 20 °C in the 1,2-dichloroethane–water system in the presence of peroxoheterotungstates and trioctylbenzylammonium chloride (TOBAC).



When the naphthol concentration is increased, C–C coupling products are formed. The catalytic system is prepared by mixing PO_4^{3}, WO_4^{2}, and TOBAC in molar proportions of 8 : 4 : 3. It is suggested that the active form of the catalyst is the peroxo-complex $PW_4O_{24}^{3-}$. The reaction proceeds via the intermediate formation of semiquinone radicals, which have been detected by the EPR method.[167]

Heteropolyacids with the Keggin structure catalyse 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 solution in acetic acid with a selectivity of 65%–78% for a TMP conversion of 94%–100%.



The hydroxylation of the benzene ring catalysed by the heteropolyacid probably results in the initial formation of 2,3,5-trimethylhydroquinone, which is subsequently rapidly oxidised to TMBQ.[168] Apparently in this case the heteropolyacid behaves as a Brønsted acid catalyst. TMP is oxidised similarly by hydrogen peroxide in the presence of sulfuric acid.[169] In acetic acid in the presence of a strong inorganic acid, H_2O_2 is rapidly converted into peracetic acid, which is probably the true hydroxylating agent.[170]

The molybdovanadium isopolyacids $H_2V_{12-x}Mo_xO_{31}$ (x = 0–4) catalyse the oxidation of 1,2,4-trimethylbenzene to TMBQ by peracetic acid in solution in acetic acid (20 °C, 4 h) with a selectivity of 12%–31% for a trimethylbenzene conversion of 15%–22%.[171]

The oxidation of ethylbenzene by hydrogen peroxide in acetonitrile in the presence of $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, and their tetrabutylammonium salts has been investigated. The main reaction product is acetophenone (selectivity 100%, PhEt conversion 5%–17%).[172]

3. Oxidation by hydroperoxides

The epoxidation of hex-1-ene by isopropylphenyl hydroperoxide (IPPHP) in isopropyl alcohol in the presence of heteropolyacid salts at 110 °C proceeds with a selectivity of approximately 100% with respect to epoxyhexane for an IPPHP conversion >80%. The rate of reaction is described by the kinetic equation $w = k[\text{HPAN}]^p[\text{IPPHP}][C_6H_{12}]$, where p = 0.5–0.9 for [HPAN] = $(0.2–9)\times 10^{-5}$ M. The catalytic activity of heteropolyacid salts decreases in the sequence $Na_3PMo_{12}O_{40} \simeq AlPMo_{12}O_{40} > Na_4PMo_{11}VO_{40} > Na_4SiMo_{12}O_{40} \gg Na_3PW_{12}O_{40}$. The heteropolyacids themselves are ineffective in epoxidation because they catalyse the decomposition of IPPHP to phenol and acetone. It has been suggested that the reaction mechanism involves the decomposition of the heteropolyanion with formation of monomeric molybdenum(VI) complexes, which are the true epoxidation catalysts.[173]

Transition metal complexes of the lacunary heteropoly-11-tungstate (p-$Bu_4N)_4HPW_{11}O_{39}M$, where M = Mn(II), Co(II), Cu(II), Fe(II), etc., catalyse the oxidation of cyclohexanol and adamantane by butyl hydroperoxide (TBHP) in benzene. The selectivity in the formation of the oxidation products (cyclohexanone or 1-adamantanol, 2-adamantanol, and 2-adamantanone) reaches 90% relative to the TBHP which has reacted. Such complexes catalyse also the oxidation of olefins (cyclohexene, hex-1-ene, norbornene, and cyclooctene) by iodosobenzene and pentafluoroiodosobenzene in acetonitrile. The manganese(II) and cobalt(II) complexes exhibit the highest activity.[174, 175]

The compound $[(C_6H_{13})_4N]_5SiW_{11}O_{39}Ru(H_2O)$ catalyses the liquid-phase oxidation of alkanes and alkenes by oxidants such as TBHP, potassium persulfate, sodium periodate, and iodosobenzene.[176]

4. Other reactions

The stoichiometric oxidation sclareol (a labdanediol) by the $PW_{11}O_{39}Tl^{4-}$ anion containing thallium(III) has been investigated. The main reaction products are epoxy-derivatives of labdane.[177]

Table 3. Acid catalysis by heteropolyacids in liquid-phase fine organic synthetic reactions (catalysts: $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, HPA/SiO_2).

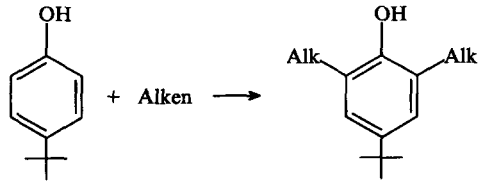
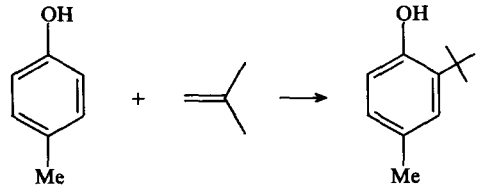
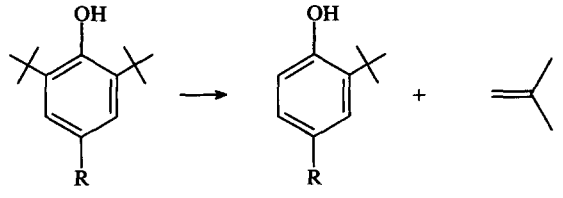
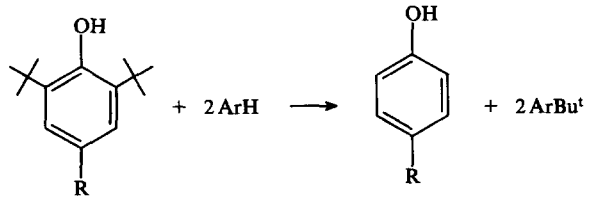
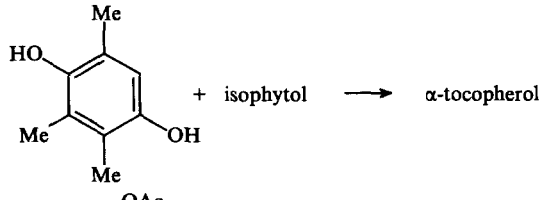
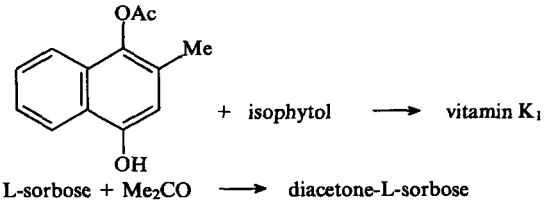
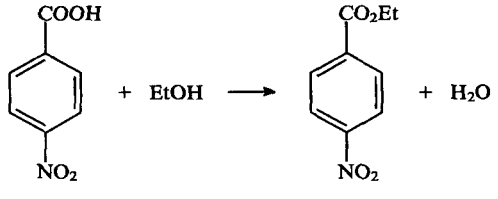
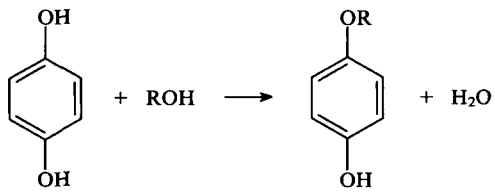
Reaction	T/ °C	Selectivity (%), (yield (%))	Ref.
(De)alkylation			
	100–150	(63–90)	68, 69
	90	80	68
	80–150	100	72–74
	100–140	(92–98)	76
Condensation			
	90–150	(92)	89
	110	(73)	89
L-sorbose + Me_2CO ⟶ diacetone-L-sorbose	56	(85)	90
Hydration			
camphene + H_2O ⟶ isoborneol	50	100	98
Esterification			
	100	99	102

Table 3 (continued).

Reaction	T/ °C	Selectivity (%), (yield (%))	Ref.
	105	99	105
monosaccaride + ROH ⟶ glycoside	85	(47–83)	107
testosterone + $(EtCO)_2O$ ⟶ testosterone propionate	40	99	108

IV. Conclusion

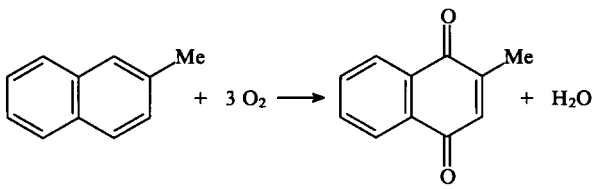
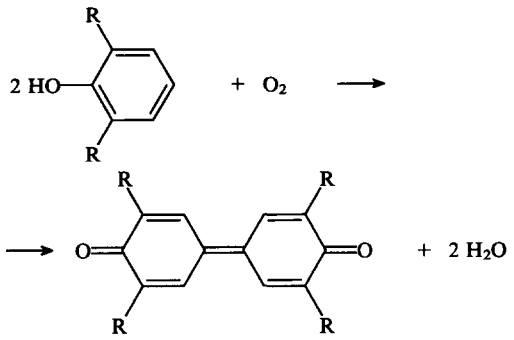
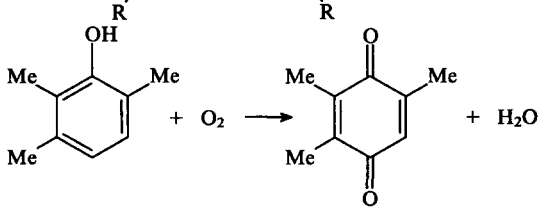
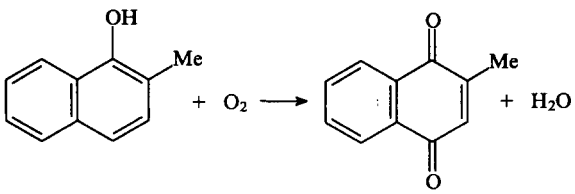
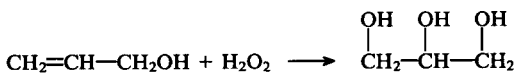
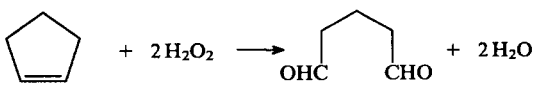
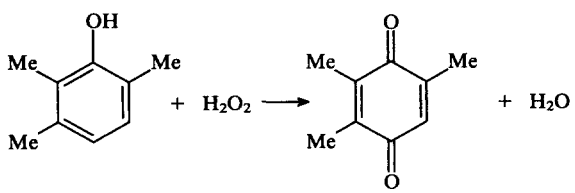
Considerable progress has been achieved during the last 20 years in the study of the catalysis by heteropolyacids. Their industrial use in organic synthetic processes has been initiated (Table 1). The employment of heteropolyacids in fine organic synthesis has given rise to considerable possibilities. The data obtained hitherto definitely indicate the likely usefulness of heteropolyacids as catalysts of fine organic synthetic reactions. Tables 3 and 4 give a compilation of the most important acid-dependent and oxidation reactions discussed in the present review. In many of them, heteropolyacids have significant advantages as regards their activity and/or selectivity compared with traditional catalysts. Some of these reactions are already being used in industry. Thus the heteropolyacid-catalysed alkylation and transalkylation of phenol derivatives is used in Russia for the synthesis of antioxidants. There are data[7] concerning the industrial application of hydropolyacids in the synthesis of glycosides in Japan. In the future the number of such processes will undoubtedly increase.

We may note the principal causes of the high effectiveness of heteropolyacid-based catalysts in organic synthesis compared with other catalytic systems. The advantages of heteropolyacids are manifested most strikingly in acid catalysis. The high effectiveness of heteropolyacids as acid catalysts is primarily due to their high Brønsted acidity, which exceeds the acidity of inorganic acids and traditional solid acid catalysts. This makes it possible to carry out the catalytic process at a lower catalyst concentration and/or a lower temperature, which tends to increase the process selectivity and permits an appreciable diminution of the amount of waste on neutralisation of the catalyst. Furthermore, by virtue of the inertness of their anions, heteropolyacids do not enter into side reactions with organic reagents, a feature typical for the usual inorganic acids (sulfonation, chlorination, nitrogenation, etc.). Heteropolyacids may be used as homogeneous or heterogeneous (massive and deposited) catalysts. In contrast to inorganic acids, heterogeneous heteropolyacid-based catalysts can be readily separated from the reaction products without neutralisation and can be reused. The heterogeneous systems are in many respects similar to concentrated solutions of heteropolyacids ('pseudoliquid phase') and exhibit a high catalytic activity in low-temperature reactions. In homogeneous systems the heteropolyacids are usually neutralised at the end of the reaction, as in the case of the inorganic acids. However, when heteropolyacids are used the amount of alkali consumed and hence the amount of waste is tens of times smaller. We may note that certain homogeneous systems divide into layers in the presence of heteropolyacids with formation of two immiscible phases, one of which contains the heteropolyacid and the other the reaction product. In such cases, the catalyst is also readily separated from the product and can be reused. Similar heterophase systems are used in the industrial polymerisation of tetrahydrofuran (Table 1)[2, 7] and in the esterification of *p*-nitrobenzoic acid with ethanol in the presence of $H_3PW_{12}O_{40}$, already noted above.[102]

The use of catalysts based on heteropolycompounds in liquid-phase oxidation reactions is also promising (Table 4). Heteropolycompounds can be employed as stoichiometric oxidants or catalysts together with oxidants such as O_2, H_2O_2, organic hydroperoxides, etc. The application of two-component catalysts incorporating transition metal complexes and a heteropolycompounds as cocatalysts appreciably expands the range of possible oxidation reactions.[3] The acid-base and oxidation-reduction properties of heteropolycompounds and the possibility of their specific regulation permit the employment of such compounds as bifunctional catalysts in processes involving coupled electron and proton transfer, which are fairly common in liquid-phase oxidation. An example of the bifunctional activity of HPC is provided by the vapour-phase oxidation of acrolein over $H_3PMo_{12}O_{40}$.[1, 2]

Much still remains to be done both in the field of fundamental research into the catalysis by HPC and in their practical employment. The unique physicochemical properties of HPC give rise to considerable potential possibilities for the investigation of the elementary steps in homogeneous and heterogeneous acid and oxidative catalysis. There is no doubt that the research into the mechanism of the catalytic activity of HPC will be continued and intensified at the molecular level with employment of HPC of different structural types. These systems are of special interest for the investigation of bifunctional catalysis and of the relation between homogeneous and heterogeneous catalysis. As regards practical application, the expansion of the research into the catalysis by HPC in fine organic synthesis, the development of new more effective methods of synthesis of HPC and catalysts based on them, methods for their isolation, regeneration, and utilisation, and the study of the corrosion activity of HPC solutions, their toxicity, etc. is of current interest.

Table 4. Liquid-phase oxidation reactions in the presence of heteropolycompounds.

Reaction	Catalyst	*T*/ °C	Selectivity (%), (yield (%))	Ref.
Oxidation by oxygen				
	HPAN-*n*	120–140	82	139
$ArH + HBr + \frac{1}{2}O_2 \longrightarrow ArBr + H_2O$	HPAN-*n*	50–100	100	127
$2\,ArH + \frac{1}{2}O_2 \longrightarrow Ar{-}Ar + H_2O$,	Pd(II)+HPAN-*n*	50–90	70–93	142–144
	HPAN-*n*	25–50	100	147
	HPAN-*n*	50–100	86	137
	HPAN-*n*	50–100	83	150
Oxidation by hydrogen peroxide				
	$H_3PW_{12}O_{40}$	70–90	64–100	151
	$H_3PMo_{10}W_2O_{40}$	35	(61)	154
olefin + H_2O_2 ⟶ epoxide + H_2O	$Q_3[PW_4O_{24}]$	70	(89)	153
olefin + H_2O_2 ⟶ glycol	$Q_3[PW_4O_{24}]$	60–70	(71–88)	158
α- or β-napthol + H_2O_2 ⟶ 1,2-naphthoquinone + H_2O	$Q_3[PW_4O_{24}]$	20	80–98	167
	$H_3PW_{12}O_{40}$	40	65–78	168
Oxidation by hydroperoxides				
hex-1-ene + ROOH ⟶ epoxide + ROH	$Na_3PMo_{12}O_{40}$	110	100	173

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