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Heteropolyacids in Catalysis

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The application of heteropolyacids (HPA) as catalysts of oxidation and acid-type reactions as well as certain physicochemical properties of the HPA important for the understanding of the mechanism of their catalytic action are examined. The mechanisms of catalytic reactions in the presence of HPA are discussed.
The bibliography includes 182 references.

CONTENTS

I. Introduction 1075
II. Certain physicochemical properties of heteropolyacids 1075
III. Heteropolyacids as liquid-phase oxidation catalysts 1080
IV. Heteropolyacids as catalysts of homogeneous reactions of the acid type 1082
V. Applications of heteropolyacids in heterogeneous catalysis 1083

I. INTRODUCTION

The application of heteropolyacids (HPA) as catalysts may be regarded as a new field in catalysis. Systematic study of this field began approximately 10 years ago, although isolated (and frequently successful) attempts to employ HPA in homogeneous and heterogeneous catalytic reactions were made even earlier. Extensive investigation of homogeneous systems based on HPA began after the discovery of the ability of molybdovanadophosphoric acids having the composition $H_{3+n}PMo^{VI}_{12-n}V_nO_{40}$ (HPA-n, where $n = 2-8$) and their salts to undergo reversible oxidation-reduction reactions in aqueous solution[1,2]:

$$\text{HPA-}n + \text{Red} + i\,\text{H}^+ \rightarrow \text{H}_i\text{HPA-}n + \text{Ox}, \quad (1)$$

$$\text{H}_i\text{HPA-}n + (i/4)\text{O}_2 \rightarrow \text{HPA-}n + (i/2)\text{H}_2\text{O}, \quad (2)$$

where Red and Ox are the i-electron reductant (the substrate or the reduced form of the cocatalyst) and its oxidised form respectively and $H_iHPA\text{-}n = H_i[H_{3+n}PMo^{VI}_{12-n}V^{V}_{n-i}V^{IV}_{i}O_{40}]$ is the heteropolyblue—the reduced form of HPA-n ($i \leq n$). The reversibility of the oxidation-reduction properties made it possible to carry out numerous oxidation reactions using HPA-n solutions as catalysts and O_2 as the oxidant[2].

Heteropolyacids have a unique set of valuable catalytic properties. They consist of polynuclear molybdenum(VI), tungsten(VI), and vanadium(V) complexes, which may also include many other elements as central atoms or ligands. HPA are many-electron oxidants and at the same time are strong Brønsted acids. The oxidation-reduction and acid properties of HPA can be varied within fairly wide limits by altering their composition. Many HPA are fairly soluble and stable in water and oxygen-containing organic solvents. At the same time they exhibit a high thermal stability in the solid state. This makes it possible to use HPA as homogeneous and heterogeneous catalysts of oxidation and acid-type reactions and also as bifunctional catalysts.

Among different HPA, the acids and their salts belonging to the saturated 12-series are of greatest importance for catalysis. They include the heteropolyanions (HPA) $X^{x}M^{VI}_{12}O^{x-8}_{40}$ or $X^{x}M^{VI}_{12-n}V^{V}_{n}O^{x-8-n}_{40}$, where X is the central atom (Si^{IV}, Ge^{IV}, P^{V}, As^{V}, etc.), x the degree of oxidation, and M the metal ion (Mo^{VI} and W^{VI}). The representatives of the 12-series are distinguished by a high stability and their properties have been investigated in detail. In this review the HPA are understood as derivatives of the 12-series unless otherwise stated. In the formulae of the HPA the H and O atoms may be omitted for brevity.

Until recently the number of studies devoted directly to the catalytic properties of HPA was less than 1% of the total number of studies on such compounds[3]. In recent years the relative contribution of these investigations increased greatly both in the USSR[2,4] and abroad[5]. This occurred as a result of the synthesis of a large number of new HPA and the accumulation of extensive information about their properties. The main contribution to the development of the chemistry of HPA was made by the schools of Spitsyn and Alimarin in the USSR, Souchay in France, and Pope in the USA.

This review deals with the results of studies on homogeneous and heterogeneous catalytic systems based on HPA carried out mainly during the last 10 years. The physicochemical properties of HPA (mainly in solutions), necessary for the understanding of the mechanism of their catalytic action, are also considered. Several short reviews devoted to the catalytic properties of HPA in homogeneous[1,2,6] and heterogeneous[7] reactions† were published previously. The synthesis, properties, and other applications of HPA of different series were examined in earlier reviews[8-14] and monographs[15,16] and the application of HPA in chemical analysis has been dealt with in two communications[17,18]. One should note that the catalytic properties of HPA are employed in a series of kinetic analytical methods (analyses for phosphorus[19] and arsenic[20]).

II. CERTAIN PHYSICOCHEMICAL PROPERTIES OF HETEROPOLYACIDS

1. The Molecular Structure of HPA of the 12-Series

Molecules of the 12-series HPA of the type $H_{8-x}X^{x}M^{VI}_{12}O_{40}$ and $H_{8-x+n}X^{x}M^{VI}_{12-n}V^{V}_{n}O_{40}$ have the Keggin structure with T_d symmetry (Fig.1), which has been established reliably as a result of numerous X-ray diffraction investigations of HPA hydrates[8-10,21-23]. This structure includes a central XO_4 tetrahedron surrounded by 12 MO_6 octahedra having common edges and vertices (O atoms). It has been frequently suggested that the MO_6 octahedra constitute a single polydentate ligand[9], but the equilibria in the degradative dissociation of HPA in solutions (see below) show that this review is not entirely justified. The radius of the HPA molecule is ~6 Å.[9] Since the ionic radius of O^{2-} greatly exceeds the radii of M^{VI} and X^{x}, the state of the O atoms in HPA is nearly close-packed[10]. The following types of chemical bonds are present in the HPA molecule: 12 quasi-linear bonds, 12 M—O—M angular bonds, 4 X—O—M bonds with bridging O atoms, and 12 M=O bonds with terminal O atoms.

†See also the review by M.Otake, J.Synth.Org.Chem. Japan, 1981, **39**, 385.

In these bonds the coordination numbers of the oxygen atom are 2,2,4 and 1 respectively. Thus the HPA contain the fundamental elements of the structures of the molybdenum, tungsten, and vanadium oxides. The HPA crystallise in the form of hydrates containing variable numbers of molecules of water of crystallisation (up to 30 and more).

2. The State of HPA in Solution. Kinetics and Mechanism of Ligand Substitution

The Keggin structure is preserved in concentrated HPA solutions but in dilute solutions ($<10^{-2}$ M) account must be taken of the degradative dissociation with ligand elimination. The retention of the Keggin structure in concentrated solutions has been demonstrated by X-ray diffraction[24-26] and by the identity of the infrared and Raman spectra of the crystals and aqueous and non-aqueous solutions of the HPA[27-31]. This is also indicated by ^{17}O NMR spectra[32-34] and the results of studies by other physical methods[35].

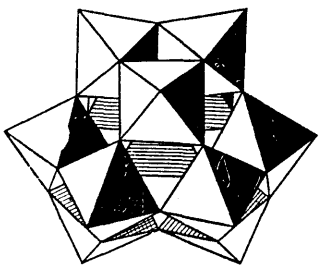


Figure 1. The Keggin structure of the 12-series HPA.[9]

By virtue of the symmetry of the anion and its large size combined with a low surface density of the negative charge, HPA and many of their salts are frequently fully dissociated in solution and the heteropolyanions are weakly solvated and behave as weak complex-forming ligands. The latter does not apply to defective heteropolyanions (HPAn), for example $SiW_{11}O_{39}^{8-}$, in which the vacancy in the Keggin structure has a high coordinating capacity[9,36,37]. The above property of the defective HPA is widely used to obtain HPA with different metal ions in the coordination sphere, for example compounds with polyanions having the general formula $XZW_{11}O_{39}^{m-}$, where X = Si^{IV}, Ge^{IV}, or P^{V} and Z = Co^{II}, Co^{III}, Ni^{II}, etc.[10].

The state of the HPA in solution is determined by the set of little investigated dissociation, disproportionation, etc. equilibria and depends on the acidity of the medium, the composition and concentration of the HPA, and the nature of the solvent. The region corresponding to their existence has been determined for a comparatively small number of HPA. The equilibration times in HPA solutions vary from a fraction of a second to several months[38].

The stability of the heteropolyanions as regards hydrolysis in aqueous solutions decreases in the sequence $W^{VI} > Mo^{VI} > V^{V}$.[10] The stability of the HPAn-Mo^{VI} decreases in the following sequence as a function of X: $Si^{IV} > Ti^{IV}$, $Zr^{IV} > Ge^{IV} > P^{V} > As^{V}$.[10] 12-Molybdophosphates exist in an acid aqueous solution at pH ≤ 1.5;[16] with increase of pH, they undergo alkaline hydrolysis, which proceeds via the following mechanism in dilute solutions ($\leq 10^{-3}$ M):[10,16]

$$PMo_{12}O_{40}^{3-} \overset{OH^-}{\rightleftarrows} PMo_{11}O_{39}^{7-} + MoO_4^{2-} \overset{OH^-}{\rightleftarrows} HP_2Mo_5O_{23}^{5-} + MoO_4^{2-} \overset{OH^-}{\rightleftarrows} HPO_4^{2-} + MoO_4^{2-}.$$

In concentrated solutions ($\sim 10^{-1}$ M) the hydrolysis proceeds via the formation of a dimeric 9-molybdophosphate $P_2Mo_{18}O_{62}^{6-}$ as an intermediate[10,16]. The polyanions with P : Mo ratios of 1 : 9, 2 : 18, and 2 : 5 predominate in the H^+–MoO_4^{2-}–HPO_4^{2-} system at pH 1.5–6.0; their stability constants have been determined[39]. In highly acidic media (pH < 1.5) the heteropolyanions undergo acid hydrolysis with formation of defective polyanions and oxomolybdenum(VI) cations[10].

The stability of HPA increases in organic media[10,12]. It has been established by the conductimetric method that acids such as PMo_{12}, PW_{12}, $SiMo_{12}$, SiW_{12}, $PMo_{11}V$, and $PW_{11}V$ are resistant to solvolysis in ethanol, acetone, and acetic acid up to concentrations in the range 10^{-6}–10^{-5} M.[40,41]. The introduction of vanadium(V) into molybdenum HPA increases their resistance to hydrolysis[42,43]. The stability of $H_{3+n}PMo_{12-n}V_nO_{40}$ (HPA-*n*) in aqueous solutions decreases with increasing *n* in the sequence HPA-1 > HPA-2 > HPA-3.[42] Although HPA-*n* with *n* > 3 have not been isolated as individual compounds[23,44], their salts are known[38,45,46]. The most stable HPA-1 begins to hydrolyse only in 0.8 M HCl.[38] The acids HPA-*n* with *n* > 1 are converted into HPA-*n* with a smaller value of *n* on increase of $[H^+]$;[43] for example, the following reaction takes place for *n* = 3:

$$10H_6PMo_9V_3O_{40} + 12H^+ \rightleftarrows 9H_5PMo_{10}V_2O_{40} + 12VO_2^+ + H_3PO_4 \quad (3)$$

The first stage of the reaction of HPA-*n* is probably degradative dissociation:

$$H_{3+n}PMo_{12-n}V_nO_{40} + H_3O^+ \rightleftarrows VO_2^+ + H_{6+n}PMo_{12-n}V_{n-1}O_{39} \quad (4)$$

At pH 1–3 the acids HPA-*n* disproportionate[43,47]

$$2PMo_{11}V \rightleftarrows PMo_{12} + PMo_{10}V_2 \cdot \quad (5)$$

The equilibrium constant of reaction (5) is 5.5×10^{-2} at pH 2.[43] The disproportionation reaction of $PW_{11}V$ is of second order with respect to $PW_{11}V$; the rate of reaction increases with pH and ionic strength *I* (the rate constants are 0.69 and 22.4 litre mol^{-1} s^{-1} at 25 °C, *I* = 3, and pH 3.9 and 4.9 respectively).[48] The heteropolyblues also disproportionate[49,50] in accordance with the mechanism

$$2PW_{11}^{VI}W^{V} \rightleftarrows PW_{12}^{VI} + PW_{10}^{VI}W_2^{V}.$$

Such reactions take place very readily and probably involve electron transfer.

The 12-series polyanions PMo_6V_6 and PMo_2V_{10} are stable in moderately acid solutions (pH 2.5–5.5).[38] Using the isotopes ^{99}Mo, ^{185}W,[51,52] and ^{17}O,[34] it was shown that the ligands in the HPA exchange with the solution. The ^{99}Mo exchange between PMo_{12} (0.01 M) and $Na_2^{99}MoO_4$ (0.1 M) in aqueous solution at 20 °C and pH 1.2 takes place to the extent of 100% in 15 min.[51] The central atom does not exchange. According to ^{17}O NMR data, the oxygen atom in the M=O, M–O–M, and X–O–M bond in HPA have markedly different chemical shifts, rates of exchange with the solvent, and degrees of protonation[32-34]. The rate of ^{17}O exchange in the HPA-*n* (*n* = 0, 1, 2) decreases by an order of magnitude following the introduction of each successive V^{V} atom into the HPA molecule. It has been suggested that the oxygen exchange proceeds via a dissociation reaction of type (4) and via ligand exchange with the solvent.

The kinetics and mechanism of the ligand substitution in heteropolyanions have been studied[53-56]. The reaction

$$VO^{2+} + SiW_{12} \rightarrow SiW_{11}V + W^{VI}$$

in aqueous solution proceeds in accordance with the kinetic equation $w = k[SiW_{12}][OH^-]$, where $k = 2.8 \times 10^6$ litre mol^{-1} s^{-1} at 25 °C. The process proceeds via a dissociative mechanism with the rate-limiting stage

$$SiW_{12}O_{40}^{4-} + OH^- \rightarrow SiW_{11}O_{39}^{8-} + W^{VI}.$$

Next vanadium(IV) is rapidly inserted in the vacancy formed[53,54]. $SiW_{11}O_{39}^{8-}$ reacts analogously with Co^{2+}, forming $SiW_{11}O_{39}Co^{6-}$.[55] In the reaction of VO^{2+} with $PW_{12}O_{40}^{3-}$ the dissociative pathway competes with the associative pathway, which includes the formation of the complex $[(HPA).VO^{2+}]$.[54]

The rate of reaction of HPA-n (n = 0–6) with VO^{2+}, i.e.

$$PMo_{12-n}V_n^V + VO^{2+} \rightleftarrows PMo_{12-n}V_{n-1}^V V^{IV} + V^V \text{ (or } Mo^{VI}), \quad (6)$$

at pH 2.2–3.0 is described by the kinetic equation $w = k[\text{HPA-}n][VO^{2+}]/[H^+]^a$, where $1 < a < 2$.[56] The formation of the intermediate complex $[(\text{HPA-}n).VO^{2+}]$ has been noted. The reactivity of HPA-n in reaction (6) varies in the sequence HPA-0 > HPA-1 > HPA-2 > HPA-3 > HPA-4 > HPA-5 > HPA-6. The mechanism of reaction (6) depends on the composition of HPA-n. The process involving HPA-0 probably proceeds via the migration of V^{IV} to the existing vacancy in the coordination sphere of the polyanion. The reaction of HPA-1 apparently involves substitution of Mo^{VI} by V^{IV}, while the inner-sphere electron transfer from V^{IV} to HPA-n is more probable in the case of HPA-n ($n > 1$).[56] The equilibrium constants of the reaction of HPA-n with VO^{2+},

$$PMo_{12-n}V_{n-i}^V V_i^{IV} + VO^{2+} + H_2O \rightleftarrows PMo_{12-n}V_{n-i-1}^V V_{i+1}^{IV} + VO_2^+ + 2H^+ \quad (7)$$

(where $0 \leq i \leq n$, n = 3.6) at pH 2.0–2.7 are almost independent of n and are approximately 10^{-6} mol^2 litre^{-2},[57] i.e. HPA-n are most resistant to hydrolysis than the corresponding blues.

The kinetics and mechanism of the formation and decomposition of heteropolyanions have been investigated[58–61]. The formation of the PMo_{12} and $PMO_{10}V_2$ anions from phosphate, Mo^{VI}, and V^V in an acid aqueous solution is very rapid[59,60]. The kinetics of these reactions are complex and their mechanism is insufficiently clear.

3. Oxidation-Reduction Properties of HPA

Many HPA are fairly strong oxidants. They are reduced by various reductants both electrochemically[10] and photochemically[62,63]. Pope[64] found an empirical rule for isopolyanions and heteropolyanions of different structures, according to which the anion is reduced without decomposition when it contains M atoms linked to one terminal O atom. Such anions include those having the Keggin ($XM_{12}^{VI}O_{40}^{x-8}$) and Dawson ($X_2M_{18}^{VI}O_{62}^{2x-16}$) structures in which each M atom has one oxo-group M=O (Pope's structural type I). The heteropolyanions decompose on reduction if each M atom has a *cis*-dioxo-group O=M=O (structural type II; $XMo_6O_{24}^{x-12}$, $Mo_7O_{24}^{6-}$, etc.). Anions containing both types of M atoms (type III; $H_2W_{12}O_{42}^{10-}$) are reduced in the same way as the heteropolyanions of structural type I. This rule makes it possible to predict the structure of the polyanion on the basis of its reducing properties.

On reduction, the HPA are converted into heteropolyblues—"mixed valence" complexes which are coloured an intense blue as a result of intervalence electronic transitions. The optical density of the blues is frequently proportional to the degree of their reduction[10,50,57,65]. Correlations have been established between the changes in the energies of the spectral bands of the blues and the half-wave potentials of the reduction of the heteropolyanions and also the charge of the heteropolyanion[28,66]. Many blues have been isolated in the form of the acids or salts.

The molecular structure of the blues has not been established rigorously. Nevertheless it is generally accepted that, for a low degree of reduction, it is the same as the structure of the initial heteropolyanions[8,9,64]. This is indicated by the identity of the X : M ratios in the blues and in the initial heteropolyanions[10,67,68], the similarity of the ultraviolet absorption spectra of the blues and the heteropolyanions[67,69], electron diffraction data[69], and also the reversibility of the polarographic reduction of many Mo^{VI}, W^{VI}, and V^V heteropolyanions[10,48–50,65,70]. The exceptional ease of the heteropolyanion reduction and oxidation reactions is apparently also a consequence of the constancy of the structure of the polyanion in oxidation-reduction reactions.

Heteropolyanions are many-electron oxidants. The limiting number of electrons accepted by the HPA molecule without decomposition depends on its composiiton and the reduction conditions: it can reach six and more electrons[49,50,65,70–72]. The addition of electrons increases the basicity of the polyanion and may be accompanied by its protonation[49,50,65,70]. The oxidative properties of HPA are closely related to their acid properties. The degree of protonation of the heteropolyanion increases with increasing basicity of the initial heteropolyanion and the degree of reduction and with decrease of the pH of the medium. These data have been obtained in the study of the dependence of the half-wave potential of the polarographic reduction of the heteropolyanions on the pH.[49,50,65,70]. The reduction of the Mo^{VI} or W^{VI} heteropolyanions can be represented by the equation

$$XM_{12}^{VI}O_{40}^{x-8} + p\,e^- + q\,H^+ \rightarrow H_qXM_{12-p}^{VI}M_p^VO_{40}^{x+q-p-8}, \quad (8)$$

where $q \leq p$. On reduction in an acid aqueous solution (pH ≤ 1), the HPAn-W^{VI} of the 12-series can have a charge up to −6 without the addition of a proton, while in a neutral medium the charge can be up to −9. The corresponding values for the more stable $X_2W_{18}O_{62}^{2x-16}$ heteropolyanions are −8 and −12.[49] The heteropolyanions are protonated preferentially on reduction at the bridging O atoms probably in the angular M–O–M linkages[73,74]. As a rule, the molybdenum and tungsten blues are more resistant to hydrolysis than the initial heteropolyanions[49].

Many studies have been devoted to the location of the added electrons in the blues[50,65,66,73–80]. According to the results obtained by spectroscopic and magnetic methods, the electrons are located in the blues at the metal ions (without the formation of a many-centre molecular orbital). There is then thermal oscillation of the electrons between all the equivalent states at frequencies $\geq 10^8$ s^{-1}; the oscillation decays at a temperature close to that of liquid helium[75,76,80]. Such oscillation probably occurs via tunnel electron transitions between the metal ions in different oxidation states.

The oxidative properties of HPA depend on the nature of both the ligands and the central atom. The standard oxidation potentials of HPA are unknown because the equilibria in their solutions have not been investigated. Instead one uses the formal potentials ϕ^0 which depend on the pH and [HPA].[11,81] The potentials ϕ^0 are considered below relative to the normal hydrogen electrode.

The oxidation potential of the HPA is lower than the potential of the ligands in the polyanion; the HPA and ligand potentials then vary in parallel. The oxidising capacity decreases in the sequences[69,82,83]

$$\text{HPA-}V^V > \text{HPA-}Mo^{VI} > \text{HPA-}W^{VI};$$
$$VO_3^- > MoO_4^{2-} > WO_4^{2-}.$$

The central constant-valence ion influences the HPA potential via a change in the charge of the polyanion[83]. The oxidation potential of the heteropolyanion decreases with increasing ionic charge in the sequence

$$PW_{12}O_{40}^{3-}(0.15) > SiW_{12}O_{40}^{4-}(-0.05) \approx GeW_{12}O_{40}^{4-}(-0.02) > BW_{12}O_{40}^{5-}(-0.36);$$

the reduction potentials (V) of the heteropolyanions at a graphite cathode in 1 M H_2SO_4 are given in brackets[76]. The oxidation potential of the HPA increases if X is a strong oxidant. Thus the reduction of $Co^{III}W_{12}O_{40}^{5-}$ to $Co^{II}W_{12}O_{40}^{6-}$ is characterised by $\phi^0 \cong 1$ V.[48,84]. The electrochemical reduction of $Fe^{III}W_{12}O_{40}^{5-}$ gives rise to a blue with Fe^{III} and not Fe^{II}.[50]

The oxidative properties of HPA-*n*, widely used as catalysts of liquid-phase oxidation, are of great interest. The introduction of vanadium(V) into HPA-Mo increases the oxidation potential of the HPA.[82,83,85]. It has been established by EPR that, on reduction of HPA-*n*, the electrons are located at the vanadium atoms[78]. The blues HPA-*n* dissociate in solution with elimination of VO^{2+}; the degree of degradative dissociation falls with decrease of *n* and with increase of pH.[86]

Fig. 2 illustrates the dependence of the HPA-*n* potential on the degree of reduction[81,87]. The reduction of HPA-*n* with $n = 1-4$ at pH 1 is characterised by a single jump of the potential $\phi^0 = 0.68-0.71$ V, which corresponds to the conversion of the entire vanadium(V) into vanadium(IV) in the heteropolyanion. The reduction process consists of a sequence of one-electron stages occurring at a single potential. The absence of individual one-electron stages can be explained by the protonation of the heteropolyanion in accordance with Eqn.(8), as a consequence of which the charge of the polyanion remains unaltered on its reduction[11]. The reduction of $PW_{12-n}V_nO_{40}^{(3+n)-}$ takes place analogously[48]. The oxidising capacity of HPA-*n* is somewhat inferior to that of the VO_2^+ ion, for which $\phi^0 = 0.87$ V at pH 1.[88] However, in contrast to the one-electron oxidant VO_2^+, the HPA-*n* is a complementary partner for one-, two-, and many-electron reductants. This makes it possible to employ the HPA-*n* as catalysts of a wide variety of oxidation reactions.

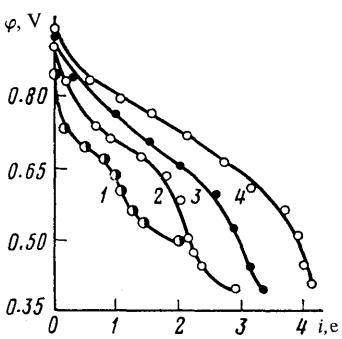


Figure 2. Dependence of the oxidation potential of HPA-*n* on the degree of reduction *i* (relative to the normal hydrogen electrode, pH 1.1, reductant—hydrazine):[81,87] *1*) $n = 1$; *2*) $n = 2$; *3*) $n = 3$; *4*) $n = 4$.

4. HPA as Oxidants Acting Reversibly

The application of HPA in homogeneous oxidative catalysis is based in many instances on their capacity for being reversibly oxidised [Eqns.(1) and (2)].[1,2] The thermodynamic condition for the occurrence of reactions (1) and (2) is

$$\varphi^0_{Red} < \varphi^0_{HPA} < \varphi^0_{O_2} = 1.23\text{V}.$$

The "mixed-ligand" HPA of structural type (I), such as HPA–Mo–V, HPA–W–V,[1,2] and HPA–Mo–W,[89] are reversibly oxidisable in the range of potentials ϕ^0 of interest for homogeneous catalysis. The HPA-*n* ($PMo_{12-n}V_n$, $n = 2-6$) have been studied in greatest detail. HPA-*n* containing at least two V atoms are reversible-action oxidants. The Mo and V heteropolyacids incorporating ligands of the same type do not have this property because their blues are hardly oxidised by the oxygen in solution. The W blues are readily oxidised by oxygen in solution[90] and are oxidised even by water (with liberation of H_2).[91] However, the HPA-W have a potential which is too low for their employment in oxidative catalysis. It is noteworthy that crystalline monometallic HPA, for example PMo_{12}, becomes reversible oxidants under more severe conditions at 200–300 °C (see Section IV).

The central atom does not exert a significant influence on the reversible oxidisability of the HPA. Furthermore, its presence is sometimes not required for the occurrence of reactions (1) and (2). For example, the mixed Mo–V isopolycompounds are reversible-action oxidants[92]. Among all the HPA having this property, the HPA-*n* are of greatest interest because of the ease of their preparation, their stability in solution, and their high reactivity.

We shall now consider the mechanism of reactions (1) and (2). It has been suggested that the true oxidants in reaction (1) are one-electron oxidants, namely the VO_2^+ ions formed as a result of the reversible dissociation reaction (4).[93] However, this mechanism is not general. The electrochemical reduction of the HPA can proceed either via successive one-electron transfers or via the simultaneous transfer of several electrons[48,49,65,70]. The oxidation of the test reagent Ph(t-Bu)CHOH by HPA-6 in aqueous solution proceeds preferentially (to the extent of 67%) via a heterolytic mechanism involving oxidation by polyanions and partly (to the extent of 33%) via a homolytic mechanism involving oxidation by VO_2^+ ions[94].

The free VO^{2+} ion is oxidised by oxygen only at pH $\geq$ 2.5. The degrees of conversion of $VOSO_4$ (0.01 M) at 14 °C after 1 week at pH 2.5 and 3.5 are 1.5 and 21% respectively[95]. In more acid media vanadium(IV) can be oxidised via reaction (2) only when it is part of the composition of the heteropolyanion. It follows from the potentials for the HPA-*n* ($\phi^0 \geq 0.68$ V) and ϕ^0 ($O_2/HO_2^\cdot$) = −0.32 V [96] that the one-electron oxidation of the blues H_i(HPA-*n*) with formation of the free radical $HO_2^\cdot$ is thermodynamically unfavourable[97–100]. The mechanism of reaction (2) depends on *i*—the degree of reduction of the blue. The blues H_i(HPA-*n*) with i, $n \geq 4$ are oxidised via the transfer of four electrons in the complex of H_i(HPA-*n*) with O_2 without the release of the free radicals into space[97–99]. For $i < 4$, free radicals are formed in reaction (2), which is indicated by the detection of acetone when reaction (2) is carried out in the presence of isopropyl alcohol[97].

The mechanism of reaction (2) was specified in detail in the study of the kinetics of the oxidation of weakly reduced blues with $i < 1$.[100] Such values of *i* are in fact usually observed in catalytic processes involving HPA-*n*. The solution of the blue then contains the anions H_1(HPAn-*n*) and HPAn-*n*. The mechanism of reaction (2) is examined below in relation to the oxidation of H_i(HPA-3).

For $i < 1$, the oxidation of H_i(HPA-3) proceeds in accordance with the kinetic equation

$$w = k[V^{IV}]^3[O_2]/[HPAn\text{-}3]^2 \qquad (9)$$

which corresponds to the mechanism

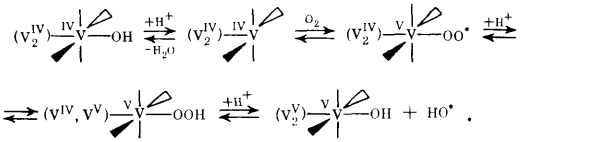
$$2PMo_9V_2^VV^{IV} \rightleftarrows PMo_9V_3^V + PMo_9V^VV_2^{IV}; \qquad (10)$$

$$PMo_9V^VV_2^{IV} + PMo_9V_2^VV^{IV} \rightleftarrows PMo_9V_3^V + PMo_9V_3^{IV}; \qquad (11)$$

$$PMo_9V_3^{IV} + O_2 + 3H^+ \xrightarrow{\text{slow}} PMo_9V_3^V + H_2O + HO^\cdot \quad (12)$$

$$PMo_9V_2^VV^{IV} + HO^\cdot + H^+ \rightarrow PMo_9V_3^V + H_2O,$$

where $PMo_9V_3^V$ = HPAn-3. Stages (10) and (11) are rapid disproportionation reactions which apparently proceed via electron transfer. The rate-limiting stage (12) includes the formation of a vacancy in the coordination sphere of H_3(HPA-*n*). Next a complex of H_3(HPA-*n*) with O_2, in which successive transfer of three electrons accompanied by the addition of H^+ takes place, is formed:



The complex of the heteropolyanion with O_2 apparently has a linear or angular structure.

The rate of oxidation of H_i(HPA-*n*) with $n > 3$ decreases in the sequence H_i(HPA-3) > H_i(HPA-4) > H_i(HPA-6), which can be explained by the increase of ϕ^0 for HPA-*n* in the same sequence (Fig.2).[100] The oxidation of H_i(HPA-2) proceeds similarly to the reaction with H_i(HPA-3) and is described by the kinetic equation (9). The process probably involves the disproportionation reaction

$$2PMo_{10}V_2 \rightleftarrows PMo_9V_3 + PMo_{11}V,$$

which is indicated by the fact that the three-electron mechanism is more favourable than the two-electron mechanism[10]. The latter has also been confirmed by the thermodynamic data for the reduction of HPA-*n* (Fig.2) and O_2.[101] The two-electron mechanism apparently operates in the oxidation of $SiW_{10}^{VI}W_2^V$ by water with evolution of hydrogen[91].

5. The Acid Properties of HPA

Heteropolyacids are strong Brønsted acids[8-10,15]. Their strength is much greater than that of simple acids formed by the corresponding heteroatoms[102]. The basicity of the HPA, which follows from the Keggin structure $H_{8-x}X^xM_{12}^{VI}O_{40}$, has been demonstrated by numerous direct measurements[10,23,85,102-104]. When Mo^{VI} or W^{VI} is substituted by V^V and on reduction of the HPA, the basicity increases by unity for each V^V ion and for each electron added. An increase of basicity is accompanied by a decrease of the acid strength of the HPA.[8-10,102,103].

Information about the proton structure of the HPA hydrates has been obtained mainly by broad-line ^1H NMR.[73,74,105-107]. Two types of protons have been found in the HPA molecules: the non-localised hydrated and localised unhydrated H^+. The former are linked to the polyanion as a whole and rapidly exchange with the protons of the water molecules in the hydration shell of the HPA. The protons of the second type appear on reduction of the HPA and on substitution of Mo^{VI} or W^{VI} by V^V. These protons are more strongly bound to the HPA and are located at the O atoms of the angular M–O–M bonds. Analogous conclusions have been reached on the basis of ^{17}O NMR data for HPA solutions[33,34].

The available acid dissociation constants of the HPA are limited as a consequence of the instability of many polyanions in solution. In aqueous solution the stepwise nature of the first three dissociations of the HPA is usually undetectable as a consequence of the levelling influence of the solvent[15,108,109]. Non-aqueous solvents have a differentiating effect on the dissociation of the HPA.[103]

According to conductimetric data, the acids $H_4PMo_{11}VO_{40}$ and $H_5PMo_{10}V_2O_{40}$ in aqueous solution are strong 1–4 and 1–5 electrolytes respectively[104]. The average $pK_{1-4} = 0.75$ was found for $H_4PMo_{11}VO_{40}$.[42] In $H_5PMo_{10}V_2O_{40}$, $H_6PMo_9V_3O_{40}$, and $H_7PV_{12}O_{36}$ the first three protons are split off completely, while the remaining are split off in steps (as the pH is increased). $pK_4 = 1.16$ and $pK_5 = 2.14$ have been found for $H_5PMo_{10}V_2O_{40}$ and $pK_4 = 1.25$, $pK_5 = 1.62$, and $pK_6 = 2.00$ have been found for $H_6PMo_9V_3O_{40}$ ($I = 0$; 25 °C).[109] $pK_4 = 3.4$, $pK_5 = 4.9$, $pK_6 = 6.4$, and $pK_7 \cong 7.9$ have been measured for $H_7PV_{12}O_{36}$ ($I = 1$; 25 °C).[108] The negative logarithms of the dissociation constants pK_5–pK_9 have been estimated for the α- and β-isomers of two six-electron blues $H_3PMo_{12}O_{40}$ from the dependence of the half-wave potential of the electrochemical reduction of the HPA on pH.[72] It was found that the α-isomers of PMo_{12} are stronger acids than the β-isomers.

Table 1. The acid dissociation constants of HPA in non-aqueous media at 25 °C and $I = 0$ (the pK_i were estimated from the Bjerrum equation).[40,41]

Acid	Acetone			Ethanol			Acetic acid	Acid	Acetic acid
	pK_1	pK_2	pK_3	pK_1	pK_2	pK_3	pK_1		pK_1
H_3PW_{12}	(1.6)	(3.0)	3.98	(1.6)	(3.0)	4.10	4.77; 4.75 [103]	H_4GeW_{12}	4.25 [103]
$H_4PW_{11}V$	(1.8)	(3.2)	4.37	—	—	—	4.74	$H_5GeW_{11}V$	4.65 [103]
$H_5PW_{10}V_2$	—	—	—	—	—	—	4.78	$H_6GeW_{10}V_2$	4.60 [103]
H_4SiW_{12}	(2.0)	3.61	(5.3)	(2.0)	3.96	(6.3)	4.97; 4.75 [103]	$HClO_4$	4.87 [113]
								HBr	5.6 [113]
H_3PMo_{12}	(2.0)	3.62	(5.3)	(1.8)	3.41	(5.1)	4.70	H_2SO_4	7.0 [113]
$H_4PMo_{11}^{VI}Mo^V$	(2.1)	3.69	(5.5)	(1.9)	3.77	(5.9)	—	HCl	8.4 [113]
$H_4PMo_{11}V$	(2.1)	3.73	(5.6)	(1.9)	3.74	(5.8)	4.68	HNO_3	10.1 [113]
H_4SiMo_{12}	(2.1)	3.90	(5.9)	—	—	—	4.78		

Note. The dissociation constant of PW_{12} in ethanol were measured conductrimetrically as in the study of Kulikov and Kozhevnikov[41]. $pK_1 = 4.0$ for HCl in acetone[88] and $pK_1 = 3.57$ for HNO_3 in ethanol[88].
The numbers in square brackets here and in Table 2 denote references (Ed.of Translation).

The acidity of the HPA has been studied more widely in non-aqueous media[40,41,103,110]. In such media the heteropolyanions are much more resistant to solvolysis[10,12]. Table 1 lists the thermodynamic dissociation constants of the HPA in ethanol, acetone, and acetic acid, measured conductrimetrically[40,41] and potentiometrically[103]. In acetone and ethanol, which are solvents of moderate polarity, the first proton of all the HPA and also the second proton in $H_3PW_{12}O_{40}$ and $H_4PW_{11}VO_{40}$ are fully dissociated at concentrations in the range 10^{-6}–10^{-3} M. The subsequent protons are only partly dissociated. In the weakly polar acetic acid the HPA behave as monobasic acids whose strength is similar to that of $HClO_4$.[40,41]

The weak dependence of the acid strength of the HPA on their composition is striking. This is due to the large size of the heteropolyanion and the unusual proton structure of the HPA.[40,41,105,109]. In aqueous and non-aqueous solutions the HPA consist of solvate-separated ion pairs $H^+(H_2O)_m \| HPAn^-$, in which the protons are hydrated and linked to the anion as a whole and not to a specific centre in the heteropolyanion[40,41]. The structure of the HPA is satisfactorily consistent with the model consisting of a

charged sphere with a large radius on the surface of which the acid protons are accommodated (with a minimal electrostatic repulsion energy) in the form of point charges[40,41].

The acidity of HPA-W is greater than that of HPA-Mo,[41,107,111] which agrees with the higher negative charge on the O atoms in HPA-Mo compared with HPA-W.[111] According to X-ray electronic spectroscopic data, the effective charges in the PMo_{12} heteropolyanion are distributed as follows: $[P^{2.5+}Mo_{12}^{1.1+}O_{40}^{0.43-}]^{3-}$.[111] The HPA are much stronger than the usual inorganic acids, which is true of both dilute and concentrated HPA solutions. The acidity of concentrated aqueous and non-aqueous $H_3PW_{12}O_{40}$ solutions (≤50 wt.%) is higher than that of $HClO_4$ and H_2SO_4 solutions by 1–1.5 units of the Hammett acidity function H_0.[112]

III. HETEROPOLYACIDS AS LIQUID-PHASE OXIDATION CATALYSTS

The liquid-phase oxidation reaction takes place in solutions in the presence of HPA-*n* or their soluble salts and more rarely other mixed HPA capable of being reversibly oxidised. The stages of the catalytic process—reactions (1) and (2)—can be carried out simultaneously in a single reactor or separately. In the latter case contact between the organic substrates and O_2 is eliminated. The catalysts may be the HPA-*n* themselves (one-component systems) or in combination with other compounds (two-component systems). Among the latter, the HPA-*n* + Pd^{II} system is of greatest importance. Homogeneous catalysts based on HPA consist as a rule of complex equilibrium mixtures of polyanions of different compositions with products of the degradative dissociation of the heteropolyanion. A common deficiency of homogeneous catalysts is the difficulty of separating the reaction products from the catalyst when high-boiling products are formed. The reactions in which the HPA-*n* are used as one- and two-component catalysts are considered below and the mechanism of their catalytic action is discussed.

1. One-Component Systems

(*a*) *Oxidation of sulphur compounds.* The oxidation of H_2S, SO_2, and mercaptans catalysed by HPA-*n* is promising for the elimination of sulphur compounds from industrial and natural gases, while the oxidation of alkyl and aryl sulphides is promising for the industrial synthesis of sulphoxides and sulphones[114–118]:

$$H_2S + 1/2O_2 \xrightarrow[H_2O,20^\circ C]{\text{HPA-}n} S + H_2O\ ; \qquad (13)$$

$$SO_2 + 1/2O_2 + H_2O \xrightarrow[H_2O,20^\circ C]{\text{HPA-}n} H_2SO_4\ ; \qquad (14)$$

$$2RSH + 1/2O_2 \xrightarrow[80^\circ C]{\text{HPA-}n} RSSR + H_2O\ ; \qquad (15)$$

$$R_2S + 1/2O_2 \xrightarrow[Me_2CO,120^\circ C]{\text{HPA-}n} R_2SO\ ; \qquad (16)$$

$$R_2SO + 1/2O_2 \xrightarrow[Me_2CO,120^\circ C]{\text{HPA-}n} R_2SO_2\ . \qquad (17)$$

In reaction (13) HPA-6 has a selectivity of ~97%; ~3% of H_2S is oxidised to H_2SO_4.[116] Reactions (16) and (17) are highly selective—up to 100% with respect to the sum of R_2SO and R_2SO_2 for a 100% degree of conversion of the sulphide[115]; on this basis, a non-radical mechanism has been proposed for these processes[115]. However, subsequent studies established that the oxidation of diethyl sulphide with $^{18}O_2$ leads to the formation of a sulphoxide enriched in the ^{18}O isotope to the extent of 44–54%. It has also been shown that, in the absence of oxygen, HPA-*n* does not oxidise Et_2S and Et_2SO to the sulphone. These data indicate a radical mechanism of reactions (16) and (17).[119]

(*b*) *Bromination of aromatic compounds.* It has been recently established[120] that HPA-*n* catalyse the oxidative bromination of arenes in the ring with participation of HBr as the brominating agent and O_2 as the oxidant. In the case of arenes, namely benzene, its derivatives, naphthalene, thiophen, etc., the process takes place in the $HOAc–H_2O–H_2SO_4$ solution at 50–100 °C and includes the following stages:

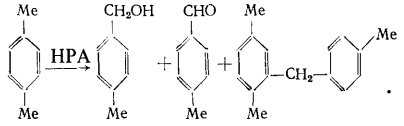
$$2HBr + HPA\text{-}n + 2H^+ \rightarrow Br_2 + H_2(HPA\text{-}n); \qquad (18)$$

$$\begin{gathered} ArH + Br_2 \rightarrow ArBr + HBr \\ H_2(HPA\text{-}n) + 1/2O_2 \rightarrow H_2O + HPA\text{-}n. \end{gathered} \qquad (19)$$

Reaction (18) takes place readily in the absence of ArH. The presence of stage (19) has been confirmed by the similarity of the isomeric compositions of the products and of the relative rates of oxidative bromination and the bromination of ArH by molecular bromine. The oxidative bromination has the advantage that one can use Br^- ions instead of Br_2 in the reaction, but it suffers from the disadvantage that the alkyl substituents in ArH are oxidised in a side reaction.

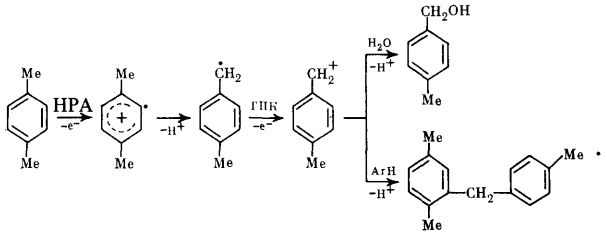
The halogenation of arenes by HCl and HI does not take place under analogous conditions, because the oxidation potential of HPA-*n* is insufficiently high for the oxidation of HCl to Cl_2; the I^- ion is readily oxidised by HPA-*n* to I_2 but I_2 is too weak as an iodinating agent.

(*c*) *Oxidation of hydrocarbons.* Heteropolyacids with a sufficiently high oxidation potential oxidise alkyl substituents in the aromatic ring[121–123]. Thus $K_5Co^{III}W_{12}O_{40}$ oxidises methylbenzenes under heterogeneous conditions in a non-catalytic process to a mixture of aldehydes, alcohols, and diarylmethanes[121]:



This reaction has been carried out catalytically using HPA-*n*.[120] In acetic acid in the presence of $K_5CoW_{12}O_{40}$ and potassium acetate, methylbenzenes undergo ring acetoxylation[123].

The proposed mechanism involves electron transfer from ArH to HPA with formation of an aromatic radical-cation whose reactions give rise to benzyl alcohol and diarylmethane[120,121]:



The alcohol undergoes further oxidation with formation of the aldehyde. When H is replaced by D in the methyl group, a large isotope effect is observed ($k_H/k_D = 6$), showing that the proton is removed from the radical-cation in the rate-limiting stage.

Heteropolyacids of different compositions have been used as catalysts of the liquid-phase oxidation of tetralin[124] and olefins[125].

(*d*) *Epoxidation of olefins by aromatic hydroperoxides.* The salts of HPA-Mo are effective catalysts of the industrially important reaction in which olefins are epoxidised by organic hydroperoxides[126–128]:

$$RCH=CH_2 + R'OOH \xrightarrow[60\sim110^\circ C]{HPA} RCH-CH_2 + R'OH \quad (20)$$

The application of the HPA themselves is undesirable because they catalyse the acid decomposition of organic hydroperoxides[129]. The mechanism of the epoxidation of olefins has been examined[128,130,131]. Molybdenum compounds are in many instances the most active catalysts. The true catalysts are probably the glycol complexes of molybdenum(VI) formed in the reaction mixture regardless of the initial ligand environment and the degree of oxidation of the metal[130,132].

The epoxidation of hex-1-ene by cumenyl hydroperoxide in isopropyl alcohol in the presence of $Na_3PMo_{12}O_{40}$ takes place without an inductive period and with a selectivity close to 100%.[133] A mechanism including rapid degradative dissociation of $PMo_{12}O_{40}^{3-}$ with formation of monomeric molybdenum(VI) and a defective heteropolyanion has been proposed on the basis of kinetic data and the study of the composition of the spent catalyst:

$$PMo_{12}O_{40}^{3-} \rightleftarrows HPAn' + nMo^{VI}.$$

The molybdenum(VI) monomers are active in reaction (20), although one cannot fully rule out also catalysis by HPAn' species. The catalytic activity of HPAn-Mo decreases slightly in the sequence $PMo_{12} > SiMo_{12} \cong PMo_{11}V$, in which the resistance of the heteropolyanion to hydrolysis increases; HPAn-Mo is much more reactive than HPAn-W.[133]

2. Two-Component Catalysts

(a) The HPA-n + Pd^{II} system. The HPAn-*n* + Pd^{II} system belongs to the class of the most important catalysts of liquid-phase oxidation based on HPA-*n*. It is highly selective in many reactions involving the oxidation of organic substances by palladium(II) salts:

$$S + Pd^{II} \rightarrow P + Pd^0, \quad (21)$$

where S and P are the substrate and reaction products. All the catalytic processes presented in Table 2 are based on a combination of reactions (21), (1), and (2) in which Red = Pd^0 and Ox = Pd^{II}. Among these, the oxidation and acetoxylation of olefins, the oxidation of alcohols, the oxidative coupling of organic compounds etc. are reactions of practical importance[1,2]. The applications and the mechanism of the action of the HPA-*n* + Pd^{II} system have been examined in a number of reviews[1,2,6,134,135].

Analogous catalytic systems based on other oxidants acting reversibly, such as Cu^{II}, Fe^{III}, NO_3^-, etc. are known[136-138]. Among them, $CuCl_2$ is of greatest importance:

$$Pd^0 + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl;$$
$$2CuCl + 1/2O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O.$$

A deficiency of the $CuCl_2$ + Pd^{II} redox system is its secondary chlorinating activity, the pronounced corrosion of the apparatus, and also the low catalytic activity of palladium(II). Like stronger oxidants, the HPA-*n* are capable of oxidising palladium(0) to palladium(II) in the absence of Cl^- ions. The HPA-*n* + Pd^{II} system is therefore free from the above deficiencies[1,2,6].

It has been established that many reactions catalysed by the HPA-*n* + Pd^{II} system proceed mainly via a multistage heterolytic mechanism with stages (21), (1), and (2).[2] Thus the oxidation of isopropyl alcohol in aqueous solution proceeds preferentially via the following stages[139,140]:

$$Me_2CHOH + Pd^{II} \rightarrow Me_2CO + Pd^0 + 2H^+;$$
$$Pd^0 + HPA\text{-}n + 2H^+ \rightarrow Pd^{II} + H_2(HPA\text{-}n);$$
$$H_2(HPA\text{-}n) + 1/2O_2 \rightarrow HPA\text{-}n + H_2O.$$

However, the radical pathway in the oxidation of the substrate, due to the intermediate formation of the $HO^\cdot$ free radicals in reaction (2), may also make an appreciable contribution under certain conditions[97,139,140], for example:

$$Me_2CHOH + HO^\cdot \rightarrow Me_2\dot{C}OH + H_2O;$$
$$Me_2\dot{C}OH + O_2 \rightarrow MeC(OH)OO^\cdot;$$
$$MeC(OH)OO^\cdot + H_i(HPA\text{-}n) \rightarrow Me_2CO + H_2O_2 + H_{i-1}(HPA\text{-}n).$$

Table 2. The liquid-phase oxidation reactions catalysed by the HPA + Pd^{II} system [Pd^{II} in the form of $PdSO_4$, $Pd(OAc)_2$, or $PdCl_2$].

Reaction	Substrate	HPA
$RCH=CH_2 + {}^1/_2O_2 \xrightarrow[H_2O]{20\sim110^\circ C} RC(O)CH_3$	C_2-C_8 α-olefins	HPA-*n* (n=2—6) [141—14]; $H_3PW_6Mo_6O_{40}$ [89]
$RCH=CH_2 + HOAc + {}^1/_2O_2 \xrightarrow[HOAc]{90\sim125^\circ C} R(AcO)C=CH_2 + H_2O$	R=H, *Me*	HPA-6 [146]
$C_2H_4 + HOAc + {}^1/_2O_2 \xrightarrow[HOAc]{20\sim40^\circ C} AcOCH_2-CH_2OH$	ethylene	HPA-6 [147]
$R_1R_2CHOH + {}^1/_2O_2 \xrightarrow[H_2O]{90\sim125^\circ C} R_1R_2C=O + H_2O$	R_1=H, R_2=Me, Pr; R_1=Me, R_2=Et; R_1, R_2=Me	HPA-*n* (n=2—6) [140, 148]
$ArH + HOAc + {}^1/_2O_2 \xrightarrow[HOAc]{90^\circ C} ArOAc + H_2O$	ArH = benzene, toluene	HPA-*n* (n=2—6) [149]
$2ArH + {}^1/_2O_2 \xrightarrow[HOAc]{50\sim90^\circ C} Ar-Ar + H_2O$	ArH = PhR (R=H, Me, Et, iso-Pr, *n*-Pr, OMe, OPh, NMe_2, Cl, COOH, CF_3), *o*-, *m*-, *p*-xylene, mesitylene, durene, thiophen, furan, sylvan	HPA-2, $H_6SiW_{10}V_2O_{40}$ [150—152]
$ArH + C_2H_4 + {}^1/_2O_2 \xrightarrow[DMF]{90^\circ C} ArCH=CH_2 + H_2O$	ArH = benzene, thiophen, furan	HPA-2, HPA-3 [153]
$R_1R_2CHCHR_3COR_4 + {}^1/_2O_2 \xrightarrow[H_2O]{60\sim70^\circ C} R_1R_2C=CR_3COR_4 + H_2O$	R_1-R_4 = H, alkyl, aryl, etc.	HPA-2 [154]

In acid solutions the oxidants for palladium(0) in reaction (1) are apparently heteropolyanions (complementary oxidation) and the VO_2^+ ions formed on dissociation of the heteropolyanion in accordance with Eqn.(4) (non-complementary oxidation).[135] The relative contributions of the heteropolyanions and VO_2^+ to reaction (1) are unknown, because the equilibrium constants of reaction (4) are not available and there are no data concerning the state of VO_2^+ in HPA-*n* solutions. The VO_2^+ ions probably form complexes with HPAn-*n*, which may influence the reactivity of VO_2^+. The question of the value of $\phi^0(Pd^{II}/Pd^0)$ has been discussed[1,6] in connection with the choice of HPA as an oxidant acting reversibly.

Apart from the HPA-*n*, other vanadium-containing HPA-Mo and HPA-W with central Si^{IV}, As^V, etc. atoms can also be used in combination with Pd^{II}.[2] It has been found recently that HPA having the composition $H_3PMo_{12-n}W_nO_{40}$ can be used as reversible-action oxidants in the oxidation of but-1-ene to ethyl methyl ketone. The catalyst incorporating $PdSO_4$ + $H_3PMo_6W_6O_{40}$ is the most active[89]. In principle there is also a possibility of employing HPA analogously in processes involving $PtCl_4^{2-}/Pt^0$ or $PtCl_6^{2-}/PtCl_4^{2-}$, but so far no examples of such reactions are known.

(b) The HPA-n + Tl^{III} system. The non-catalytic oxidation of unsaturated hydrocarbons by thallium(III) salts is used widely in preparative organic chemistry[155]. The

reactions cannot be catalysed because of the difficulty of oxidising thallium(I) to thallium(III) with oxygen. The possibility of oxidising thallium(I) to thallium(III) with oxygen in the presence of copper(II) and iron(III) halides has been noted in a number of patents[156,157].

It has been found that HPA-*n* (n = 2–8) easily oxidise thallium(I) to thallium(III) in aqueous acid or aqueous acetic acid solutions in the presence of Br^- ions[158]. The role of the Br^- ions reduces to diminishing $\phi^0(Tl^{III}/Tl^I)$ as a result of the formation of the thallium(III) bromide complex:

$$TlBr + HPA\text{-}n + 2HBr \rightarrow TlBr_3 + H_2(HPA\text{-}n). \quad (22)$$

Since H_2(HPA-*n*) is rapidly oxidised by oxygen, the HPA-*n* + $TlBr_3$ system can serve as a catalyst of the oxidation of organic substances by oxygen. An example of such a reaction is provided by the bromination of C_6–C_8 olefins with formation of dibromoalkanes and bromohydrins[158]. Further studies of the HPA-*n* + Tl^{III} redox system with other ligands, ensuring the formation of oxygen derivatives of the substrate being oxidised, are desirable.

(*c*) *The HPA-n + Ru^{IV} and HPA-n + Ir^{IV} systems.* Alkanes are oxidised by HPA-6 in aqueous solution in the presence of ruthenium(IV) and iridium(IV) chloride complexes (pH 1; 100–120 °C).[159] The oxidation of propane yielded acetone. The rate of oxidation of the t-C–H bond is higher than that of the s-C–H bond. The reaction mechanism has not been investigated, but it is probably analogous to the mechanism of the oxidation of alkanes by the Cr^{VI} + Ru^{IV} system[159].

(*d*) *The HPA-n + I_2 system.* The ability of I_2 to add rapidly and reversibly to the double bond of an olefin and the ease of the oxidation of I^- to I_2 by HPA-*n* constitute the basis of the application of the HPA-*n* + I_2 system in the oxidation of olefins to glycol ethers[160]:

$$CH_3CH{=}CH_2 + HOAc + 1/2O_2 \xrightarrow[HOAc]{HPA\text{-}6+I_2} \underset{OAc}{\overset{}{CH_3CH}}\!\!-\!\!\underset{OH}{\overset{}{CH_2}} .$$

The catalytic process can be represented by the following stages:

$$CH_3CH{=}CH_2 + I_2 + H_2O \rightleftarrows \underset{I}{\overset{}{CH_3CH}}\!\!-\!\!\underset{OH}{\overset{}{CH_2}} + HI; \quad (23)$$

$$\underset{I}{\overset{}{CH_3CH}}\!\!-\!\!\underset{OH}{\overset{}{CH_2}} + HOAc \rightarrow \underset{OAc}{\overset{}{CH_3CH}}\!\!-\!\!\underset{OH}{\overset{}{CH_2}} + HI; \quad (24)$$

$$2HI + HPA\text{-}6 \rightarrow H_2(HPA\text{-}6) + I_2; \quad (25)$$

$$H_2(HPA\text{-}6) + 1/2O_2 \rightarrow HPA\text{-}6 + H_2O. \quad (26)$$

Stage (24) is apparently rate-limiting[160]. Instead of HPA-*n*, it is possible to use also other oxidants acting reversibly. The most active catalyst is $CuCl_2$ + I_2; here copper(II) acts as an electrophile in collaborating in the elimination of the halogen from the carbon atom in stage (24).[160] The catalysis by metal complexes in halide ion elimination reactions has been examined[161].

IV. HETEROPOLYACIDS AS CATALYSTS OF HOMOGENEOUS REACTIONS OF THE ACID TYPE

The likely usefulness of the HPA as acid catalysts is determined by their high Brønsted acidity. In aqueous solutions which level off the acidities of strong acids, the HPA have no significant advantages over the usual inorganic acids. However, in non-aqueous media which differentiate acidities, the HPA proved to be much more effective than inorganic acid, because under such conditions their acidities are higher. In reactions of the acid type oxidising properties are usually harmful, since the acidity of the HPA is lowered when they are reduced. The HPA-W are therefore preferable to the HPA-Mo, because the former compounds are stronger acids and weaker oxidants than the latter.

1. Hydration and Esterification of Olefins

The hydration of olefins constitutes an industrial method of synthesising alcohols (particularly ethanol and isopropyl alcohol):

$$RCH{=}CH_2 + H_2O \overset{H^+}{\rightleftarrows} \underset{OH}{\overset{}{RCHCH_3}} . \quad (27)$$

The reaction is carried out at an elevated pressure ensuring the displacement of equilibrium (27) to the right. The application of the HPA-W on solid carriers as heterogeneous catalysts of the hydration of olefins has been known for a long time[162,163]. Thus $H_4SiW_{12}O_{40}$ and $NaH_3SiW_{12}O_{40}$ (10^{-5}–10^{-3} M) catalyse the hydration of C_2–C_4 olefins in aqueous solution at temperatures in the range 170–350 °C and pressures in the range (1–5) × 10^4 kPa.[164] The reaction is carried out in the presence of silicic acid at a concentration of 0.5–4.5 g litre^{-1}, which increases the stability and activity of the catalyst. The process selectivity reaches 95–99% and the alcohol content in the reaction mixture is 8–12%.

The analogous reaction of C_3–C_{20} olefins in solution in carboxylic acids in the presence of 10^{-4}–10^{-2} M HPA-Mo or HPA-W at 20–140 °C leads to the formation of esters[165,166]:

$$RCH{=}CH_2 + HOAc \xrightarrow{HPA} \underset{OAc}{\overset{}{RCHCH_3}} . \quad (28)$$

The selectivity of reaction (28) reaches 100% for a 90% conversion of the olefin.

The formation of 2-hexyl acetate from hex-1-ene solution in acetic acid proceeds in accordance with the kinetic equation:

$$w = k_1[HPA][C_6H_{12}] - k_{-1}[HPA][ester],$$

where k_1 = 0.23 litre mol^{-1} s^{-1} and k_1/k_{-1} = 6.2 for $H_3PW_{12}O_{40}$ at 110 °C.[167] Since the HPA are weak acids in solution in acetic acid ($pK_1 \cong 5$),[41] the first order term in HPA shows that the reaction proceeds via general acid catalysis by undissociated HPA molecules. The catalytic activity of the HPA is almost independent of their composition and is ~100 times higher than the activity of H_2SO_4, which agrees well with the dissociation constants of the acids in acetic acid (Table 1). In the course of reaction (28), the HPA-Mo are appreciably reduced and for this reason their values of k_1 are lower than for the HPA-W.

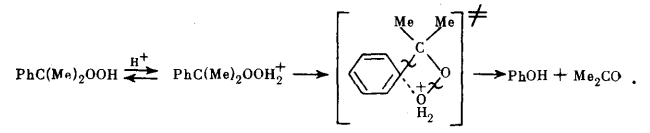
2. The Composition of Alkylphenyl Hydroperoxides

This important reaction constitutes the basis of the industrial method of the joint synthesis of phenol and acetone. It is catalysed by many HPA-Mo and HPA-W:[129,168,169]

$$PhC(Me)_2OOH \xrightarrow[40\rightarrow90\,^\circ C]{HPA} PhOH + Me_2CO . \quad (29)$$

Reaction (29) proceeds with a quantitative yield in solution in acetone or in an equimolar mixture of phenol and acetone for [HPA] = 0.01–0.08 wt.%. The selectivity of the HPA is so high that the phenol obtained does not require purification before its subsequent hydrogenation to cyclohexanol in the presence of the palladium catalyst[168].

The acid decomposition of alkylphenyl hydroperoxides proceeds via the protonation of the peroxy-group and subsequent synchronous rearrangement in the cyclic transition state (see Kozhevnikov and Kulikov[128] and the references quoted therein):



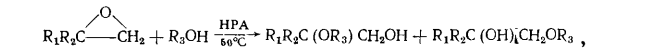
Reaction (29) in acetone in the presence of $H_3PMo_{12}O_{40}$ proceeds via the mechanism of general acid catalysis:

$$w = (k_H[H^+] + k_A[H_3PMo_{12}O_{40}^-])[ROOH] .$$

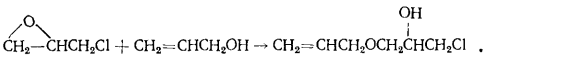
$k_H = 4.5$ litre mol^{-1} s^{-1} and $k_A = 14$ litre mol^{-1} s^{-1} were obtained at 25 °C.[129] Under the conditions indicated, the acid $H_2PMo_{12}O_{40}$ has a fully dissociated first proton and partly the second proton[40]. The main contribution comes from the $k_H[H^+]$ specific acid catalytic pathway. The catalytic activity of the HPA in acetone varies in parallel with their dissociation constants and is higher by a factor of 10^3 than the activity of H_2SO_4. HPA on γ-Al_2O_3 also catalyse reaction (29), but the activity of the heterogeneous catalyst is much lower than that of the homogeneous catalyst[129].

3. Other Reactions of the Acid Type

The acids PW_{12}, PMo_{12}, and SiW_{12} are effective homogeneous catalysts of the alcoholysis of epoxides with formation of hydroxyethers:

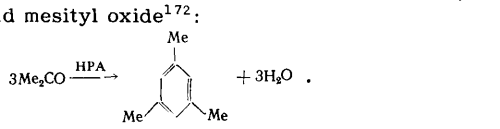


where R_{1-3} = H, alkyl, or aryl[170]. In the presence of an excess of the alcohol the polymerisation of epoxides does not take place. On interaction with allyl alcohol, epichlorohydrin gives rise to 1-allyloxy-3-chloro-2-propanol in 95–97% yield:



The reaction is of first order with respect to epichlorohydrin and the HPA. The strongest acid PW_{12} is also the most active catalyst among the HPA investigated; H_2SO_4 and $HClO_4$ are less effective than the HPA.

The acids $H_{8-x}X^xM_{12}O_{40}$ (X = Si^{VI} or P^V; M = Mo^{VI} or W^{VI}) on a solid carrier or in solution catalyse the condensation of alkyl ketones to aromatic compounds[171,172]. In the presence of a heterogeneous catalyst, the reaction requires severe conditions (200–450 °C, 7×10^3 kPa).[171] The homogeneous condensation proceeds under milder conditions. Thus in a solution of 40 wt.% HPA in acetone at 25 °C, aromatic hydrocarbons (mesitylene and other alkylbenzenes) are obtained at 25 °C in the course of 1–10 days in 40–55% yield relative to the reacted ketone in a mixture with water, methyl acetate and mesityl oxide[172]:



The degree of conversion of acetone is 25–45% and the catalyst can be used repeatedly.

In the presence of the HPA as homogeneous or heterogeneous acid catalysts, other reactions of practical importance also take place, such as the alkylation of aromatic compounds by olefins[173], the carbonylation of alcohols, the synthesis of formic acid from CO and water[174], the oligomerisation of olefins[175], etc.

V. APPLICATIONS OF HETEROPOLYACIDS IN HETEROGENEOUS CATALYSIS

Heteropolyacids and their salts have been used for a long time as heterogeneous catalysts in various oxidative and acid processes of practical importance. The studies up to 1975 have been briefly considered in a number of reviews[7,10,15]. It has recently become clear that heteropolycompounds are also of great interest for fundamental research into heterogeneous catalysis[2,176]. By altering the composition of the HPA, it is possible to vary independently and within wide limits their oxidising and acidic properties and also to achieve bifunctional catalysis. The constancy of the structure and the similarity of many physicochemical properties of the HPA in crystals and in solution (see below) permit the employment of the ideas concerning the mechanism of homogeneous catalytic reactions of the HPA for the analogous heterogeneous catalytic reactions.

HPA hydrates in the form of massive specimens are usually employed in heterogeneous catalysis. They are frequently deposited (10–15 wt.%) on solid carriers (SiO_2, Al_2O_3, etc.). Many HPA exhibit a fairly high thermal stability. For example, the acids PW_{12}, SiW_{12}, PMo_{12}, and $SiMo_{12}$ have average decomposition temperatures of 465°, 445°, 375°, and 350 °C respectively[107]. It is significant that the thermal stability of the HPA greatly increases in the presence of water vapour[177], but there are few quantitative data concerning this question.

The HPA hydrates behave in many respects similarly to solutions, which enables one to expect an analogy between the mechanisms of the action of the homogeneous and heterogeneous HPA-based catalysts. The behaviour of the HPA as a "pseudoliquid phase" [176] is manifested primarily in the mobility of structural elements. In the HPA hydrates, the polyanions are not linked to one another; the regularity of the packing is achieved as a result of the formation of hydrogen bonds with the molecules of the water of crystallisation[9,10]. According to ^{31}P NMR data, in the PW_{12} and PMo_{12} acid hydrates with a high water content the heteropolyanions rotate fairly readily at a frequency $\geq 10^3$ Hz [178] and their acid protons exchange rapidly with the protons of the water of crystallisation[73,74,105,106]. Even in anhydrous HPA the structural elements migrate freely at temperatures in excess of 150 °C. The activation energy for the self diffusion of H^+ decreases with increasing acid strength and amounts to 78.5, 54.6, 44.1, and 29.4 kJ mol^{-1} for PW_{12}, SiW_{12}, PMo_{12}, and $SiMo_{12}$ respectively. Small amounts of added water vapour accelerate the self diffusion of H^+.[107] The oxygen atoms in the M=O and M–O–M bonds in crystalline HPA exchange with water, as in solutions[176]. The rate of exchange of oxygen in the HPA is appreciably higher than in metal oxides. Thus 80% of the oxygen in PMo_{12} is exchanged in the course of 1 h at 250 °C, while only 0.4% is exchanged in MoO_3 in the course of 1.5 h at 440 °C.[176]

The adsorption of pyridine on massive specimens of the HPA PMo_{12}, PW_{12}, and $SiMo_{12}$ has been studied[176,177]. It has been established that the entire adsorbed pyridine exists in the form of the ion $C_5H_5NH^+$, i.e. the acidity of the HPA is of the Brønsted type. The amount of pyridine per HPA molecule is equal to the basicity of the HPA and is independent of the fact that part of the heteropolyanion is inaccessible to pyridine vapour. Thus not only surface

protons but also protons belonging to the heteropolyanion and located within the bulk of the specimen react with pyridine, similarly to reactions in solution[176]. The acidity of the crystalline HPA has been little investigated; according to the available data[107,176], the acidities of the HPA in the solid state and in solutions vary equally with their composition.

At 200–250 °C, $H_3PMo_{12}O_{40}$ is reduced by hydrogen. On subsequent treatment with molecular oxygen, the reduced form is reoxidised to the initial state. Such oxidation-reduction transformations of PMo_{12} are fully reversible for the addition (in the reduction process) of two electrons by an HPA molecule, but become irreversible when the degree of reduction corresponds to the addition of five electrons[176]. The analogy between the oxidation-reduction properties of solid HPA and the properties of the HPA-*n* in solutions can be seen in this example (see Section III).

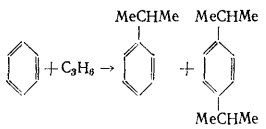
There have been several new studies of the application of the HPA in heterogeneous acid and oxidative catalysis and of the mechanism of their catalytic action. Like zeolites, the HPA-W catalyse the conversion of methanol into hydrocarbons[179]. Such reactions are of great interest in connection with the problem of the synthesis of an artificial liquid fuel from CO and H_2. In the presence of PW_{12} in a flow-type reactor at 245–357 °C and at atmospheric pressure, a mixture of olefins and alkanes ranging from C_1 to C_7 as well as traces of CO and CO_2 are formed. At 245 °C the mixture contains 43% of the butane–butene and 27% of the pentane–pentene fractions. The selectivity with respect to these products decreases with increase of temperature. A mechanism analogous to that of the corresponding reactions in the presence of superacids in solution has been proposed:

$$MeOH + H^+ \rightarrow Me^+ + H_2O\,,$$

$$Me^+ + MeOH \rightarrow \left[\begin{array}{c} H \\ Me^+ \end{array}\right\rangle\!\!\cdots CH_2OH \rightarrow MeCH_2OH + H^+\,;$$

$$MeCH_2OH \rightarrow C_2H_4 + H_2O\,.$$

The very active catalyst of the alkylation of benzene by propene (the first stage of the cumene process of the synthesis of phenol and acetone) is 40% $H_4SiW_{12}O_{40}/SiO_2$:[173]



(30)

The reaction proceeds at 150 °C, 15×10^2 kPa, and $[C_6H_6]/.[C_3H_6] = 4$ with a selectivity of 72.5% with respect to isopropylbenzene for a propene conversion of 97.5%. The lifetime of the catalyst is 500 h. Di-isopropylbenzene is returned to the system to be transalkylated. The SiW_{12} HPA has virtually the same parameters as the aluminosilicate catalyst—one of the best heterogeneous catalysts of reaction (30). However, the latter operates under more severe conditions (300 °C and 3×10^3 kPa). In the alkylation process the catalysts are gradually saturated with coke and require regeneration; the coke is burnt off in a stream of air. After regeneration, the aluminosilicate catalyst has the previous activity and stability, but the HPA does not withstand severe regeneration conditions—it is dehydrated and loses activity irreversibly. This example demonstrates the urgent need for the development of new methods of regenerating HPA-based catalysts which do not reduce their activity.

The kinetics of the dehydration of isopropyl alcohol in the presence of HPA have been studied by a flow method[176]. The steady-state rate of reaction at 100 °C, referred to the catalyst surface, decreases in the following sequence of HPA: $PW_{12} > SiW_{12} > PW_{10}V_2 > PMo_{12} > PMo_{10}V_2 \cong SiMo_{12}$, and in the following sequence of their salts: $H_3PW_{12}O_{40} > Na_2.HPW_{12}O_{40} > Na_3PW_{12}O_{40}$. The catalytic activity of the HPA is satisfactorily correlated with their dissociation constants in acetone (Table 1).

The mechanism of the oxidation of methacrolein (RCHO) to methacrylic acid has been investigated in the presence of water vapour ($p_{H_2O} \cong 40$ kPa) at 280–300 °C.[176] The catalysts were massive HPA and their salts. The HPA-Mo (PMo_{12}, $SiMo_{12}$) and their copper(II) and caesium salts proved to be the most active and selective. The tungsten(VI) compounds have a lower activity and selectivity. In a flow reactor at 300 °C in the presence of PMo_{12} the reaction proceeds with a selectivity of 74.4% and a conversion of the substrate of 16.6%. Acetic acid (2.3%), Co (11.9%), and CO_2 (11.4%) are also formed. Water plays an important role in this reaction: in the absence of water, the selectivity and conversion are much lower. The process proceeds in accordance with the kinetic equation

$$-\mathrm{d}[RCHO]/\mathrm{d}\tau = kp_{RCHO}^{(0.6-1.0)}p_{O_2}^{(0.6-0.2)}p_{H_2O}^{0}\,. \qquad (31)$$

The process selectivity hardly changes after the cessation of the supply of O_2 under the conditions of the steady-state activity of the catalyst, which shows that the reaction proceeds in accordance with the oxidation-reduction mechanism via the following stages:

$$RCHO + HPA + H_2O \rightarrow RCOOH + H_2(HPA); \qquad (32)$$

$$H_2(HPA) + \tfrac{1}{2}O_2 \rightarrow HPA + H_2O\,. \qquad (33)$$

It follows from the kinetic equation(31) that stage (32) is rate-limiting. The mechanism described by reactions (32) and (33) is also supported by the rapid exchange of ^{18}O between acroleine and PMo_{12} at 300 °C.[176]

In principle, using HPA it is possible to achieve bifunctional oxidative and acid catalysis, but this interesting application of the HPA has so far been only slightly investigated. It has been established that, together with the oxidative properties of the HPA, their acidity plays a significant role in the oxidation of methacroleine, which has been confirmed by the poisoning of the catalyst by added pyridine[176]. The bifunctional catalysis by the HPA probably occurs in the oxidative hydration of propene to acetone[180].

Among new and promising but hitherto little investigated applications of HPA in heterogeneous catalysts, one should mention their employment for the synthesis of catalysts having a specified composition. All or some of the components of the catalyst can then be incorporated in the heteropolycomplex as ligands, central atoms, or outer-sphere cations. The complex is then deposited on a carrier and is subjected to a chemical or thermal treatment in order to obtain the final catalyst. This method has significant advantages over the successive deposition of the components. It reduces the number of stages in the preparation of the catalyst and ensures a very intimate mixing of the components (up to mixtures at the molecular level) starting from the heteropolycomplex, which is much more difficult and sometimes impossible to achieve by other methods. Studies[181,182] in which the formation of HPA on the surface of a solid carrier during the synthesis of heterogeneous catalysts by traditional methods was observed are of interest in this connection. Thus the silica–molybdenum oxide catalyst for the oxidation of propene, obtained by the spray drying of an aerosil suspension in an ammonium paramolybdate solution, contains molybdosilicic acid which determines the activity of the catalyst in the oxidation of propene. The HPA obtained in stable up to 500–600 °C as a result of stabilisation by the SiO_2 surface.

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