

$\text{PMo}_{12-n}\text{V}_n\text{O}_{40}^{(3+n)-}$ heteropolyanions as catalysts for aerobic oxidation

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Abstract

Recent applications of Keggin-type heteropolyanions $\text{PMo}_{12-n}\text{V}_n\text{O}_{40}^{(3+n)-}$ (HPA-*n*) as catalysts for aerobic liquid-phase oxidation are reviewed. Discussed are HPA-*n* catalyzed reactions in homogeneous, biphasic, and heterogeneous systems as well as mechanistic aspects of the HPA-*n* catalysis.

Keywords: Heteropolyanions; Catalysts; Oxidation; Dioxygen

1. Introduction

Catalysis with polyoxometalates (POM) is a field of growing importance [1–5]. These compounds, having well-defined structures and remarkable acid–base and redox properties, attract increasing attention worldwide.

The purpose of this paper is to review recent applications of Keggin-type heteropolyanions $\text{PMo}_{12-n}\text{V}_n\text{O}_{40}^{(3+n)-}$ (HPA-*n*) as catalysts for aerobic liquid-phase oxidation. The HPA-*n* catalytic system, discovered by Matveev et al. in the 70s [6], is the most efficient and versatile catalyst system in the POM series for oxidation by O_2 [7–9]. A HPA-*n* based catalyst is used in industry for the heterogeneous gas-phase oxidation of methacrolein to methacrylic acid [3].

Structurally, HPA-*n*, as well as many other heteropolyanions important for catalysis, be-

longs to the best known and most stable Keggin series. They have a well-known Keggin structure which is composed of a central PO_4 tetrahedron surrounded by 12 randomly distributed MoO_6 and VO_6 metal–oxygen octahedra [10] (Fig. 1). For the preparation of HPA-*n*, see [5–8].

2. General principles

In liquid-phase oxidation, HPA-*n* with *n* = 2–6 are used. These compounds are remarkable because they are reversibly acting oxidants under mild conditions [6,7]. The presence of a certain number of V ions in the heteropolyanions is essential. Thus, the all-molybdenum anion $\text{PMo}_{12}\text{O}_{40}^{3-}$ (HPA-0) fails to possess such redox properties under mild conditions; so does HPA-1 for reasons that will be discussed later.

Generally reactions catalyzed by HPA-*n* pro-

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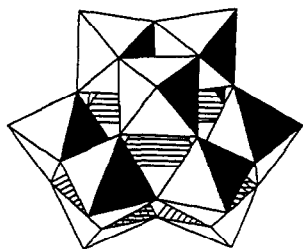
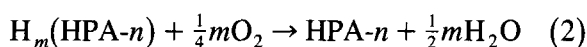
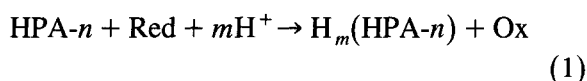


Fig. 1. The Keggin structure of HPA- n (α -isomer).

ceed via a stepwise Mars–Van Krevelen-type mechanism,



This mechanism includes stoichiometric oxidation of the substrate (Red) by HPA- n followed by reoxidation of the reduced form of the oxidant, $\text{H}_m(\text{HPA-}n)$, with dioxygen, where $\text{H}_m(\text{HPA-}n) = \text{H}_m(\text{PMo}_{12-n}^{6+}\text{V}_{n-m}^{5+}\text{V}_m^{4+})^{(3+n)-}$, $m \leq n$. Actually, it is the $\text{V}^{5+} \rightleftharpoons \text{V}^{4+}$ transformation that is responsible for the redox properties of HPA- n . The reduction of HPA- n in solution is accompanied by its protonation to maintain the charge of the polyanion [10].

Reactions (1) and (2) can be carried out in the same reactor (one-stage process) or separately as a combination of two stoichiometric reactions (two-stage process) [6,7]. Thus HPA- n combines the advantages of stoichiometric and catalytic oxidations.

As the catalysts, either one-component or two- and multicomponent systems are used. The most important two-component system includes HPA- n and Pd(II). Other two-component systems are also known, e.g. those including complexes of Pt, Ir, Ru, Tl, etc. [7].

The thermodynamic condition for the occurrence of reactions (1) and (2) is: $E(\text{Red}) \leq E(\text{HPA}) \leq E(\text{O}_2) = 1.23 \text{ V}$ [7]. The oxidation potential $E(\text{HPA})$ is 0.68–0.71 V versus normal hydrogen electrode for HPA- n with $n = 1$ –4 at pH 1 [11]. Hence the above condition fulfills for a wide variety of organic substrates as well as

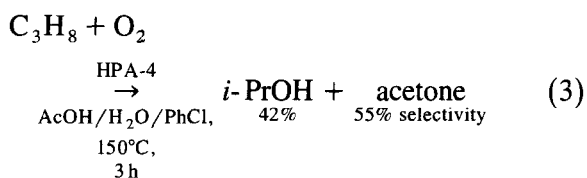
for many inorganic redox systems to be used as cocatalysts with HPA- n .

3. Catalytic reactions

3.1. Homogeneous oxidation

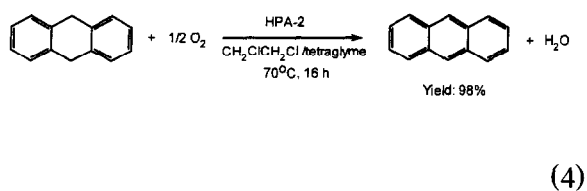
3.1.1. One-component HPA- n system

A range of hydrocarbons can be homogeneously oxidized with HPA- n as catalyst under mild conditions. Thus HPA- n catalyzes the oxidation of alkanes to oxygenates by O_2 [12],

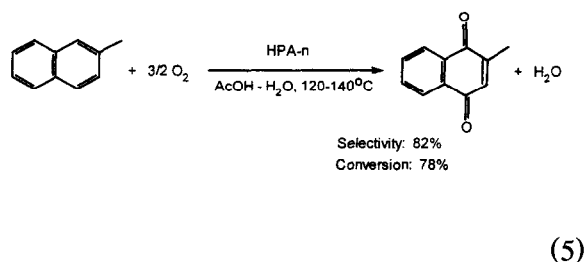


The mixed-addenda HPA- n are more efficient catalysts than the all-molybdenum heteropolyanions.

Many synthetically attractive oxidations of hydrocarbons have been developed to date. For example, highly efficient dehydrogenation reactions with HPA-2 in $\text{CH}_2\text{ClCH}_2\text{Cl}$ /tetraglyme solution have been reported by Neumann et al. [13],

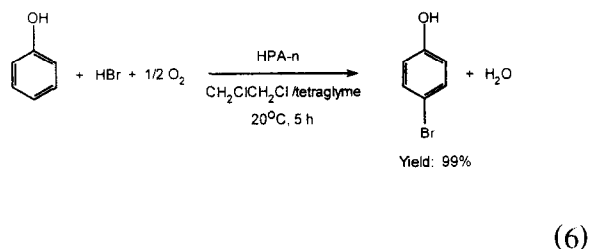


Oxidation of 2-methylnaphthalene to quinone,

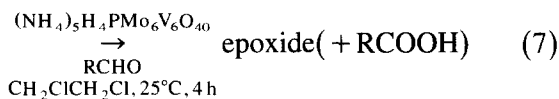


is a step of the vitamin K₃ synthesis. In industry it is carried out with highly toxic CrO₃ as a stoichiometric oxidant with a low yield. With HPA-*n*, we have succeeded to carry out the catalytic oxidation in a higher yield [14].

Oxidative bromination of a range of aromatics catalyzed by HPA-*n* has been reported with HBr as a brominating agent and O₂ as a terminal oxidant [15]. More recently Neumann et al. [16] reported the oxidative bromination of phenols in the para-position with a remarkably high yield,

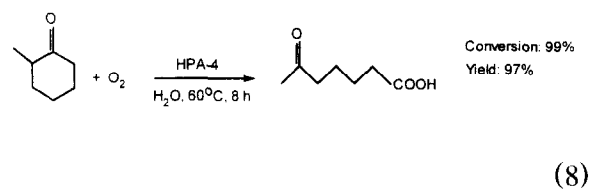


Ishii et al. [17] have studied a number of interesting oxidations with O₂ in the presence of an aldehyde as sacrifice and HPA-*n* as catalyst. Thus the epoxidation of olefins proceeds at room temperature with a very high selectivity, alkene + O₂

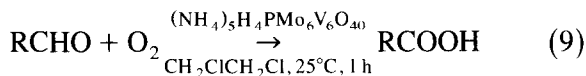


(selectivity: 81–100%). A carboxylic acid as a cooxidation product is also formed. This may be synthetically useful if the carboxylic acid is a useful product.

A variety of oxygenates, e.g. aldehydes, ketones, phenols, etc., can be oxidized with HPA-*n* under mild conditions with very good yields. Brégeault et al. [18] reported the oxidative cleavage of cyclic ketones,

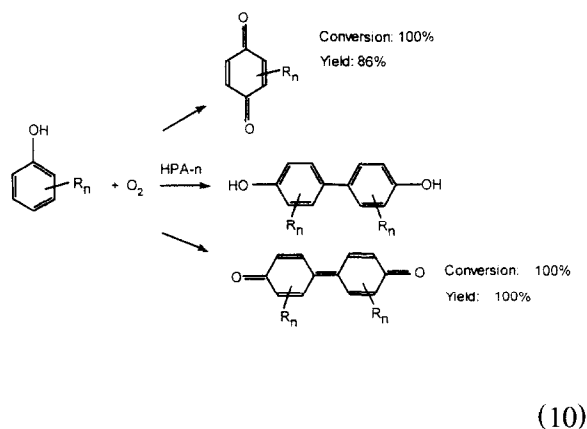


Ishii et al. [17] studied the oxidation of aldehydes to carboxylic acids with the use of the NH₄⁺ salt of HPA-6 as catalyst,



(conversion: 60–78%, selectivity: 96–100%).

We [19,20] and also Neumann et al. [21] reported synthetically attractive oxidations of alkylphenols (Eq. (10)): the oxidation of 2,3,5-trimethylphenol (TMP) to trimethylbenzoquinone (TMBQ) which is of practical interest as a step to synthesize vitamin E; and the oxidative coupling of 2,6-dialkylphenols to diphenoquinones which can be used for the synthesis of antioxidants.

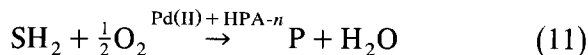


Oxidation of sulfur compounds can be efficiently carried out with HPA-*n*. For example, the oxidation of H₂S to sulfur [22] and thioethers to sulfoxides and sulfones [23] proceeds with nearly 100% yield.

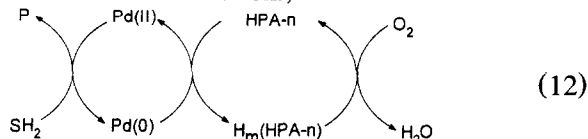
3.1.2. Two-component system HPA-*n* + Pd(II)

The two-component redox system HPA-*n* + Pd(II), discovered by Matveev [6,24], has attracted considerable attention. A wide variety of stoichiometric oxidations of organic compounds (SH₂), e.g. olefins, alcohols, arenes, etc., by Pd(II) can be carried out catalytically with the

use of HPA-*n* as a cocatalyst and O₂ as an oxidant [4,7,8,25],



Generally, such reactions proceed via a stepwise redox mechanism,

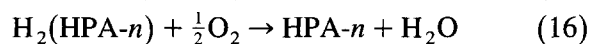
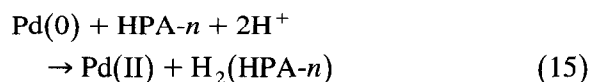
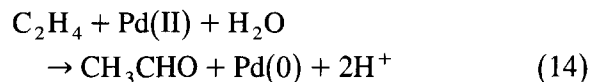


It is analogous to the Wacker-type oxidation with CuCl₂-PdCl₂ as the catalyst. But the HPA-*n* + Pd(II) catalyst can work in the absence or at a very low concentration of Cl⁻ ions. That is why it has the advantage of being more selective and less corrosive [6].

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



The Wacker process is industrially employed for manufacturing acetaldehyde from ethylene and acetone from propylene [26]. The CuCl₂ + PdCl₂ redox system is used as a catalyst. However, this process has several drawbacks such as formation of chlorinated byproducts and strong corrosion of the reaction vessel. So the development of chloride-free oxidants to replace CuCl₂ has long been a challenge. Matveev [6,24] first proposed the use of HPA-*n* as chloride-free oxidant in the Wacker reaction. The oxidation of ethylene can be represented by the following equations:



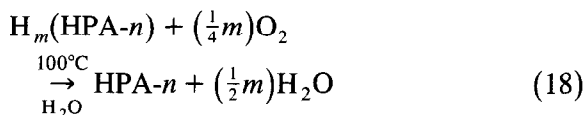
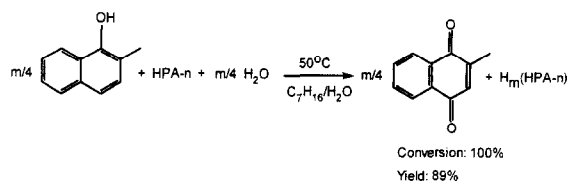
Catalytica [8] has recently developed new technology for the Wacker oxidation of ethylene and higher olefins with the use of the HPA-*n* + Pd(II) system. In order to enhance the reaction

rate and to stabilize Pd(II) in solution, the reaction is carried out in the presence of Cl⁻ ions at a very low concentration (5–25 mM). In this process, over 99% of the production of chlorinated byproducts is eliminated, decreasing to less than 0.01% yield on ethylene.

3.2. Biphasic reactions

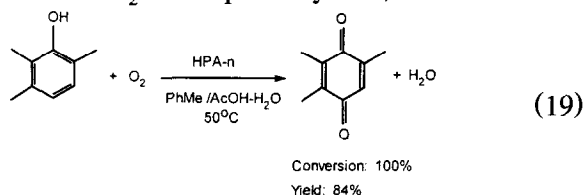
The advantage of biphasic systems is that they combine a catalytic reaction and product separation in one unit. POMs, due to their special solubility properties, offer interesting opportunities for this. It is especially promising for fine and specialty chemicals synthesis to avoid difficult separation problem.

Matveev et al. [27] reported two-stage oxidation of 2-methyl-1-naphthol to menadione in a high yield with space-separated steps (17) and (18), step (17) being carried out in an aqueous-hydrocarbon two-phase system,

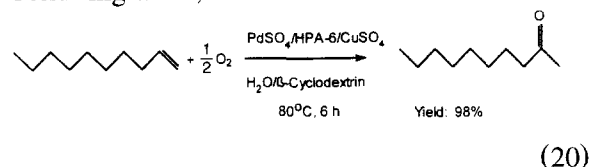


This is a promising alternative to the conventional synthesis of vitamin K₃ by oxidizing 2-methylnaphthalene with CrO₃.

We [28] have developed the efficient one-stage oxidation of TMP to TMBQ in an ArH-AcOH-H₂O two-phase system,



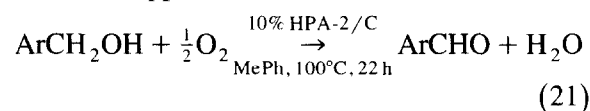
Monflier et al. [29] reported the biphasic Wacker oxidation of 1-decene to 2-decanone with excellent yield and practically no double bond migration,



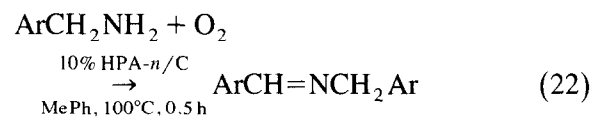
In this case a three-component catalyst system is used, containing Pd(II), HPA-6 and Cu(II), where Cu(II) is suggested to promote the Pd reoxidation. The key point about this is the use of a cyclodextrin as a phase-transfer catalyst, which transfers 1-decene to the aqueous phase by a host-guest interaction.

3.3. Heterogeneous reactions

Heterogenized HPA-*n* catalysts have attracted considerable interest. Both liquid-phase and gas-phase reactions have been studied. Neumann et al. [30] reported the liquid-phase oxidation of benzylic compounds (Eqs. (21) and (22)) with excellent yields with one-component HPA-*n* system supported on activated carbon, which very strongly adsorbs POM. This catalyst has also been applied for the oxidation of TMP [31].



(yield: 94–98%)

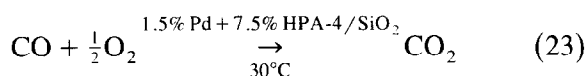


(yield: 100%).

Considerable attention has been paid to the heterogeneous two-component Pd(II) + HPA-*n* system, especially regarding gas-phase Wacker oxidation and related reactions. As a support, silica is generally used, which is relatively inert towards POM. There are two main problems in applying this system to the gas-phase oxidation: (1) the reoxidation of the catalyst by O₂ pro-

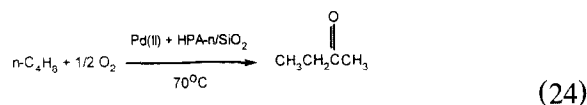
ceeds much slower than in solution and (2) the catalyst rapidly becomes inactive due to aggregation of palladium.

The oxidation of CO to CO₂ was reported by Matveev et al. [32],



The Pd(II) + HPA-*n* catalyst was found to be more active than Pd/TiO₂ and Pd/SiO₂. But eventually the catalyst exhibited irreversible deactivation.

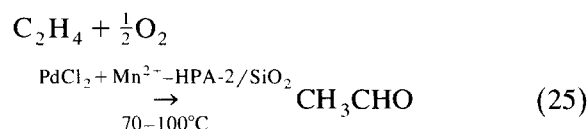
The heterogeneous oxidation of butene to methylethylketone is the most challenging goal [33,34]. It has recently been studied with both HPA-*n* and their Cu²⁺, Ni²⁺, Pd²⁺ and Cs⁺ salts [33],



Conversion: 60% → 6% after 1 h
Selectivity: 98% → 90%

However, very strong deactivation was observed: the conversion dropped ten-fold after 1 h on stream.

Yet very recently quite a stable activity after 50 h on stream has been obtained in the ethylene oxidation with the catalyst promoted by Mn²⁺ [35],



(conversion: 80%, selectivity: 98%).

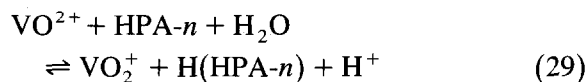
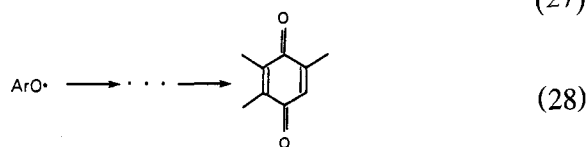
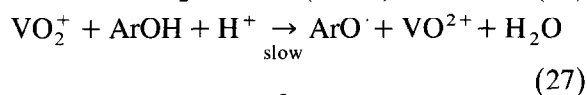
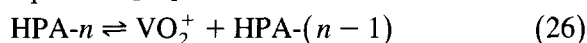
It should be noted that reactions (23)–(25) are all carried out in the presence of steam. Mechanistically they can be considered as pseudohomogeneous, i.e. occurring in the liquid catalyst phase entrapped in the support.

4. Mechanistic aspects

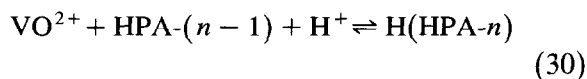
HPA-*n* in solution is an extremely complex system, and the higher the *n* value is, the more

complex the system. The HPA-*n* solutions contain a great number of iso- and heteropolyanions, their positional isomers as well as monomeric vanadium oxocations [7,8]. This makes mechanistic studies very difficult. Much work has been done on characterization of the HPA-*n* solutions [7,8]. Recently Pettersson et al. [36] have fully characterized the HPA-2 solutions by potentiometry and ^{31}P and ^{51}V NMR. This is a relatively simple and stable system, which is used in Catalytica's new technology for Wacker oxidation of olefins [8]. It consists of five positional α -isomers and some β -isomers of $\text{PMo}_{10}\text{V}_2\text{O}_{40}^{3-}$ which have been identified by ^{31}P and ^{51}V NMR.

As said earlier, the overall catalytic process can be represented by steps (1) and (2). The question is what is the mechanism of these steps? What kind of active species is involved? In step (1), two types of active species can be considered [7]. First, the monomeric VO_2^+ cation and/or complexes thereof, which is formed via the dissociation of parent HPA-*n*. It is likely for HPA-*n* with higher *n* and in strong acidic media. For example, there is evidence that the monomeric VO_2^+ is the active species in the oxidation of TMP (ArOH) (Eq. (19)). Such a mechanism can be represented by the following equations [20]:

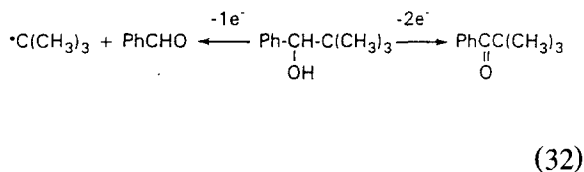


or



The rate-determining step is probably one-electron oxidation of the phenol by VO_2^+ to form the phenoxy radical (Eq. (27)). Subsequent transformations of the phenoxy radical give quinone. V^{4+} formed in the reaction returns into the heteropolyanion either by an electron transfer (Eq. (29)) or by association with the lacunary species HPA- $(n-1)$ (Eq. (30)). Eventually, V^{4+} is reoxidized by O_2 inside HPA-*n* (Eq. (31)). It should be noted that the free VO^{2+} ion is not oxidized by O_2 in acidic solution.

Secondly, parent heteropolyanions can be the active species in step (1) [7]. It is likely in the case of the more stable polyanions with fewer V ions (e.g. HPA-2). As the heteropolyanions are multielectron oxidants, they can, in principle, react via a multielectron-transfer mechanism. In this sense, the oxidation of a test alcohol *t*-Bu(Ph)CHOH is of interest [37],



With two-electron oxidants, e.g. Pd(II), this alcohol gives a ketone (Table 1). With one-electron oxidants, e.g. Ce^{4+} and persulfate, the C–C bond cleaves to yield benzaldehyde. It is seen that VO_2^+ reacts as one-electron oxidant, as expected. In contrast, HPA-6 predominantly acts as a two-electron oxidant, giving the ketone in 67% yield; simultaneously the one-electron oxidation probably by VO_2^+ ions also takes

Table 1
One- versus two-electron oxidation of *t*-Bu(Ph)CHOH^a

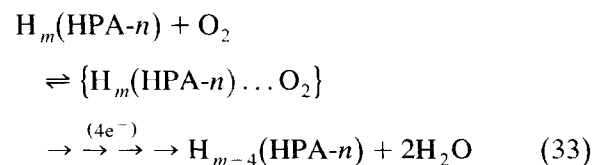
	Oxidant				
	PdCl ₂	Ce ⁴⁺	S ₂ O ₈ ²⁻	VO ₂ ⁺	PMo ₆ V ₆ O ₄₀ ⁹⁻
Ketone (%)	100	6	6	11	67
PhCHO (%)	—	94	89	63	33

^a Yields (mol%) on converted alcohol; a little PhCOOH is also formed.

place to give benzaldehyde (33%). This may be indicative of the heteropolyanion intermediacy in reaction (32).

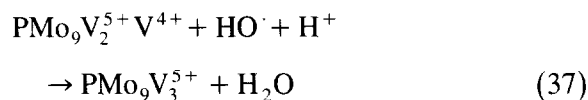
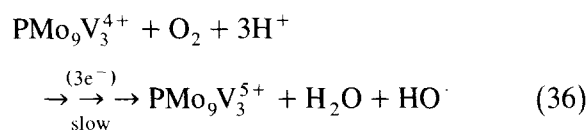
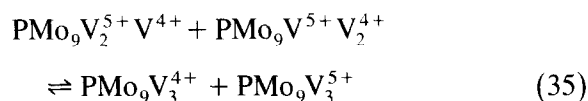
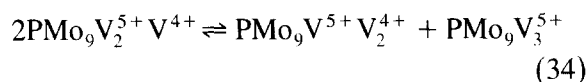
Much research has been done on the mechanism of oxidation of the reduced form of HPA- n ('blue') by O_2 (Eq. (2)). For a review, see [7]. It should be noted that the one-electron oxidation of blue to form the $HO_2\cdot$ radical is highly unfavorable thermodynamically. That is why the HPA-1 blue, $PMo_{11}V^{4+}O_{40}^{4-}$, is practically not oxidized by O_2 under mild conditions in solution. The all-molybdenum HPA-0 blue is not oxidized either. For this reason, HPA- n with $n > 1$ are used as catalysts in low-temperature oxidations. It is noteworthy that the reoxidation of HPA-0 and HPA-1 by O_2 proceeds readily at higher temperatures, e.g. $> 200^\circ C$. Under such conditions, they are widely used for heterogeneously catalyzed gas-phase oxidations, e.g. oxidation of methacrolein and oxidative dehydrogenation of isobutyric acid. For a review, see [1,3].

It was found that the mechanism of step (2) depends on the degree of reduction of blue. Two systems were studied. The first one is a deeply reduced blue with $n \geq 4$, all the V present being reduced to V^{4+} [38]. This practically never happens in real catalytic reactions, but it is a very convenient model system. In this system, the reaction follows a simple kinetics: first order in both the blue and O_2 . In the presence of a radical scavenger, i -PrOH, no acetone was found. So no free radicals are formed. Hence a 4-electron-transfer mechanism was proposed. The mechanism includes the formation of a complex between the blue and O_2 followed by a stepwise 4-electron transfer therein [38],

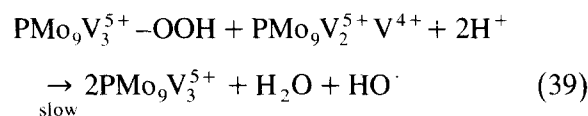
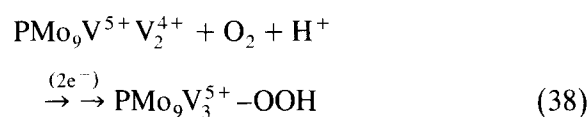


The second system is a weakly reduced blue (by less than 1 electron per Keggin unit) [39].

This system is adequate to real catalytic systems and shows a more complex behavior. The reaction was found to be third order in V^{4+} , minus second in the parent HPA- n and first in O_2 . The test with i -PrOH clearly showed the formation of free radicals. On these bases, a 3-electron-transfer mechanism was proposed, which is represented for HPA-3 by the following equations:



In steps (34) and (35), a 3-electron blue is formed by the fast electron exchange between 1-electron blues. Then the 3-electron blue is slowly oxidized by O_2 via a 3-electron transfer to form the $HO\cdot$ radical, which is finally trapped by any V^{4+} species [39]. Alternatively, the reaction can include the fast 2-electron oxidation to form hydroperoxo intermediate (step (38) instead of (35)) followed by a slow 1-electron transfer step (39) to give the $HO\cdot$ radical. This easily explains the reoxidation of HPA-2 blue.



Further, it was found that the free radicals generated in step (2) can, to some extent, affect the selectivity of the one-stage catalytic process [40]. But obviously, they do no harm in the case of the two-stage process.

5. Conclusion

HPA-*n* is the efficient and versatile catalyst system for oxidizing by O₂. Several promising processes based on HPA-*n* have been developed, e.g. the Wacker oxidation of olefins. Principal mechanistic features of HPA-*n* catalyzed reactions have been documented, although many details are yet to be disclosed.

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