

# Catalytic Oxidation of Organic Compounds with Oxygen in the Presence of Mo–V–Phosphoric Heteropoly Acid Solutions

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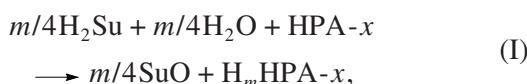
**Abstract**—The studies carried out at the Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, on the selective catalytic oxidation of organic compounds with oxygen in the presence of aqueous solutions of Mo–V–phosphoric heteropoly acids (HPAs) are reviewed. Alkylphenols are oxidized into 1,4-quinones with a selectivity of 85–99%, and C<sub>2</sub>–C<sub>4</sub> olefins in the presence of Pd complexes are oxidized into carbonyl compounds with a selectivity of 98–99%. The bifunctional (acidic and oxidizing) properties of HPA solutions were used for the first time to synthesize anthraquinones and vitamin K<sub>3</sub>.

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In the early 1970s, the Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, for the first time suggested using aqueous solutions of Mo–V–phosphoric heteropoly acids (HPAs) as components of catalysts for oxidation of various organic compounds with oxygen [1, 2]. Keggin-type HPAs of composition H<sub>3+x</sub>PV<sub>x</sub>Mo<sub>12-x</sub>O<sub>40</sub> (HPA-*x*, *x* = 2–6) are conventionally used in these processes.

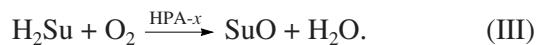
Oxidation in the presence of HPA-*x* has quickly attracted researchers' attention round the world. A number of reviews have been devoted to these reactions (see, e.g., [3–9]). Furthermore, natural interest in the structure of aqueous solutions of HPA-*x* has arisen. <sup>31</sup>P and <sup>51</sup>V NMR spectroscopy have become the basic method in these studies [10, 11].

Catalytic oxidation reactions in the presence of HPA-*x* solutions consist of steps (I) and (II). In the first of them, the substrate (H<sub>2</sub>Su) is oxidized by HPA; in the second, the reduced form of HPA-*x* is reoxidized with molecular oxygen:



In these reactions, H<sub>*m*</sub>HPA-*x* is the reduced form of HPA-*x* having composition H<sub>3+x+m</sub>PV<sub>*m*</sub><sup>IV</sup>V<sub>*x-m*</sub><sup>V</sup>Mo<sub>12-x</sub>O<sub>40</sub>, where *m* is the number of vanadium(IV) atoms in H<sub>*m*</sub>HPA-*x* and can vary discretely from 0 to *x*. Thus, vanadium atoms take part in homogeneous redox reactions (I) and (II) and the HPA-*x* compounds are reversibly acting oxidizers (RAOs). In this respect, they are advantageous over irreversible oxidizing agents, such as CrO<sub>3</sub>, KMnO<sub>4</sub>, and NaIO<sub>4</sub> [12].

The overall process of H<sub>2</sub>Su oxidation by oxygen in the presence of HPA-*x* is described by the equation

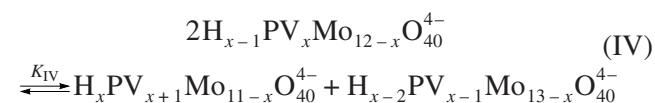


In principle, process (III) can be carried out in one step. However, in order to increase selectivity (and, in some cases, for the sake of explosion safety), it is usually carried out in two steps in different reactors. Below, we will consider our data concerning the high-selectivity oxidation of substrates of various classes with oxygen in HPA-*x* solutions.

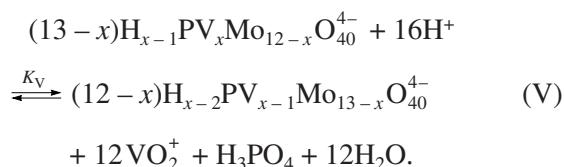
## COMPOSITION OF SOLUTIONS OF HPA-*x* AND THEIR REDUCED FORMS

To characterize steps (I) and (II), it is necessary to discuss, at least briefly, the structure of aqueous solutions of HPA-*x*. At *x* = 1, the Keggin structure allows the existence of a single isomer, HPA-1. At *x* > 1, there can be several HPA-*x* isomers, whose number is 5 for *x* = 2, 13 for *x* = 3, 27 for *x* = 4, 38 for *x* = 5, and 48 for *x* = 6 [13]. Therefore, a number of isomer anions H<sub>*x-1*</sub>PV<sub>*x*</sub>Mo<sub>12-x</sub>O<sub>40</sub><sup>4-</sup> (HPA-*x*) are always present in aqueous solutions of HPA-*x* at *x* > 1. This is indicated by “paling” of narrow lines in the <sup>31</sup>P and <sup>51</sup>V NMR spectra of these solutions [14, 15].

In HPA-*x* solutions, anions undergo a number of reversible conversions. These include the disproportionation reaction

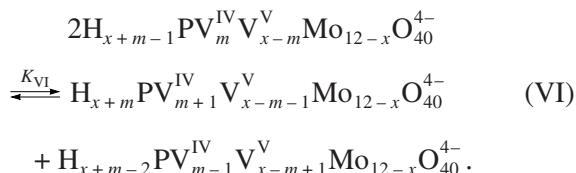


and protolysis occurring in strong acid media to yield free  $\text{H}_3\text{PO}_4$  and  $\text{VO}_2^+$  cations:



The resulting  $\text{H}_3\text{PO}_4$  and  $\text{VO}_2^+$  show themselves in  $^{31}\text{P}$  and  $^{51}\text{V}$  NMR spectra as broad lines overlapped with the narrow lines of heteropoly anions [10, 16].

The composition of partially reduced HPA- $x$  solutions is more complicated. They contain  $\text{H}_{x+m-1}\text{PV}_m^{\text{IV}}\text{V}_{x-m}^{\text{V}}\text{Mo}_{12-x}\text{O}_{40}^{4-}$  (HPA- $x_m$ ) anions with various values of  $m$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{VO}_2^+$  and  $\text{VO}_2^+$  cations [17, 18]. In these solutions, the reversible disproportionation of anions takes place:



For characterization of  $\text{H}_m\text{HPA-}x$  solutions in catalytic processes, the average value  $m^*$ , calculated as the average degree of reduction of the solution,

$$m^* = [\text{V}^{\text{IV}}]_{\Sigma}/[\text{H}_m\text{HPA-}x] \quad (1)$$

is very important. In this formula, the concentration of  $\text{H}_m\text{HPA-}x$  is equal to the initial concentration of HPA- $x$ . The value of  $m^*$  increases from 0 to  $m_{\text{max}}^* \leq x$  during reaction (I) and decreases to  $m_{\text{min}}^*$  during HPA- $x$  regeneration [19, 20]. The changes in  $m^*$  are easy to monitor by measuring the redox potential ( $E$ ) of the solution, which decreases during the reduction of HPA- $x$  and increases during the oxidation of  $\text{H}_m\text{HPA-}x$  [21].

### REGENERATION OF AQUEOUS HPA- $x$ SOLUTIONS VIA REACTION (II)

This step is common for all of the oxidation processes (III). Moreover, it is the key step in the implementation of these processes.

Our thermochemical studies [22, 23] have shown that the heat of reaction (II) (or its enthalpy  $-\Delta_f H_{\text{II}}$ ) is variable. For solutions of lower HPA- $x$  ( $x = 1-3$ ),  $-\Delta_f H_{\text{II}}$  decreases monotonically with a decreasing  $m^*$ . For solutions of HPA- $x$  with  $x = 4-6$ ,  $-\Delta_f H_{\text{II}}$  at  $m^* \geq 2.8$  is comparatively constant and is 306 kJ/(mol  $\text{O}_2$ ). At these values of  $m^*$ , the oxidation of HPA- $x_{m \geq 3}$  anions, containing no fewer than three vanadium(IV) atoms in the coordination sphere, takes place. At smaller  $m^*$  values, the other V(IV)-containing species are oxidized and  $-\Delta_f H_{\text{II}}$  is lower [23]. Thermochemical data have con-

firmed the complete reversibility of the changes in the composition of the HPA- $x$  solutions during reduction and oxidation according to reactions (I) and (II).

The kinetics of reaction (II) is very complicated [24]. At atmospheric pressure and  $T < 373$  K, the initial oxidation rate of  $\text{H}_m\text{HPA-}x$  solutions with  $x \geq 3$  is high; for  $x = 2$  it is much lower, and  $\text{H}_m\text{HPA-}1$  solutions are not oxidized with oxygen at all [25]. As  $m^*$  decreases, the oxidation rate of  $\text{H}_m\text{HPA-}4$  decreases by a factor larger than 100. In the initial (fast) region, at high values of  $m^*$ , reaction (II) has low apparent activation energy ( $E_a \sim 10$  kJ/mol) and is first-order with respect to  $\text{O}_2$  and  $\text{H}_m\text{HPA-}x$ . In the slow region ( $m^* < 2$ ), the order of the reaction with respect to  $\text{H}_m\text{HPA-}x$  increases to 2.8, a sharp deceleration of the reaction by  $\text{H}^+$  ions is observed, and  $E_a$  increases up to  $\sim 200$  kJ/mol [24]. As a result, at low temperatures ( $\sim 303$ – $323$  K), the oxidation of  $\text{H}_m\text{HPA-}x$  does not reach completion. For example, a 0.2 M solution of  $\text{H}_m\text{HPA-}4$  is oxidized only to  $m^* \sim 1.6$  at 313 K and to  $m^* \sim 1.2$  at 343 K [25].

This sophisticated behavior is explained by the change of the rate-limiting step of reaction (II). At  $m^* > 2.8$ , the rate of the reaction is determined by the rate of the interaction of the HPA- $x_{m \geq 3}$  anions with oxygen:

$$w_{\text{II}} = k[\text{HPA-}x_{m \geq 3}][\text{O}_2]. \quad (2)$$

As  $m^*$  decreases, the solution being oxidized is progressively depleted in HPA- $x_{m \geq 3}$  anions and  $w_{\text{II}}$  begins to be controlled by the rate of their formation from HPA- $x_{m \leq 2}$  [24].

For the most complete oxidation of  $\text{H}_m\text{HPA-}x$  solutions at low values of  $m^*$ , it is necessary to raise the temperature of reaction (II) as high as possible. The optimum parameters are  $T = 423$ – $433$  K and  $P_{\text{O}_2} = 4$  atm. Under these conditions, the  $m_{\text{min}}^*$  value of the  $\text{H}_m\text{HPA-}x$  solution can be reduced to  $\sim 0.45$  for  $x = 4$  and to  $\sim 0.25$  for  $x = 2$  [26]. Thus, even the 0.2 M solution of  $\text{H}_m\text{HPA-}2$ , which oxidizes slowly at  $T < 373$  K and  $P_{\text{O}_2} < 1$  atm, can be oxidized rather quickly and deeply at elevated temperatures under  $\text{O}_2$  pressure [27]. The maximum regeneration temperature is determined by the thermal stability of the HPA- $x$  solution, which depends on  $x$  and on the HPA- $x$  concentration [20].

### SOLUTIONS OF MODIFIED HPA- $x$

The productivity of a catalyst in step (I) is proportional to the product  $\Delta m^*$  [HPA- $x$ ], where  $\Delta m^* = m_{\text{max}}^* - m_{\text{min}}^*$ . Therefore, to ensure high efficiency, concentrated (0.25–0.30 M) solutions of high-vanadium HPA- $x$  ( $x = 4-6$ ) are necessary. However, when operating at elevated temperatures (up to 433 K), solutions of Keggin-type HPA- $x$  form vanadium-containing deposits. As this takes place, the total vanadium concentration participating in redox processes (I) and (II) decreases, causing a decrease in the catalyst productivity.

It was possible to create thermally stable and workable oxidation catalysts only after obtaining solutions of Mo–V–phosphoric HPAs of modified compositions [28–30]. These compositions differ from the Keggin compositions and are described by the formula  $H_aP_zMo_yV_{x'}O_b$  (HPA- $x'$ ), where  $1 \leq z \leq 3$ ,  $8 \leq y \leq 20$ ,  $1 \leq x' \leq 12$ ,  $40 \leq b \leq 89$ , and  $a = 2b - 6y - 5(x' + z)$  [20, 29]. Some HPA- $x'$  solutions have a high thermal stability: they do not form deposits during long-term operation at  $T \sim 443$  K. The total vanadium concentration in these solutions can reach 2.5 mol/l, which is three times higher than that in 0.2 M HPA-4.

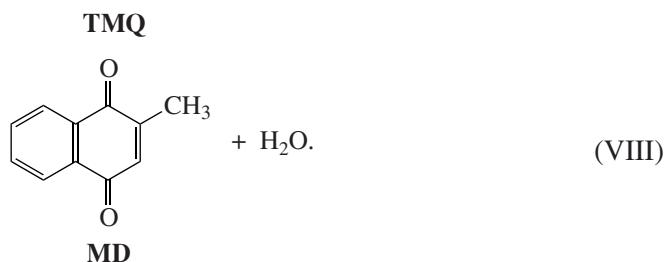
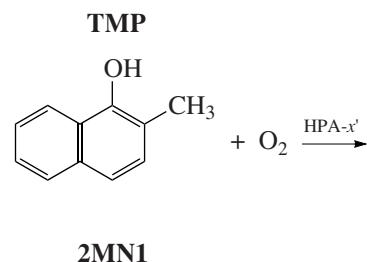
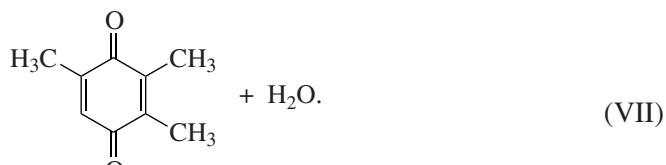
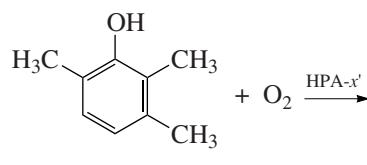
Owing to the high vanadium(V) concentration, the redox potential of the modified HPA- $x'$  solutions is substantially higher than that of the HPA- $x$  solutions. During the reduction of HPA- $x'$  via reaction (I), the  $E_{\text{HPA-}x'}$  decreases considerably more slowly than  $E_{\text{HPA-}x}$  (figure). This makes the catalysts based on HPA- $x'$  solutions more efficient in oxidation reactions. For this reason, the thermally stable modified solutions of HPA- $x'$  ( $x' \geq 6$ ) were used in the processes described below.

It was shown by  $^{31}\text{P}$  and  $^{51}\text{V}$  NMR that the modified HPA- $x'$  solutions are equilibrium mixtures as compli-

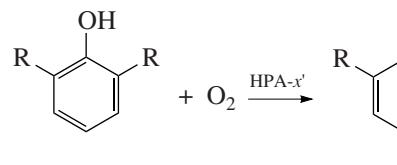
cated as the HPA- $x$  solutions. They contain  $H_{x-1}\text{PV}_x\text{Mo}_{12-x}\text{O}_{40}^{4-}$  anions ( $x = 1-4$ ) with a Keggin structure,  $\text{H}_3\text{PO}_4$ , and  $\text{H}^+$  and  $\text{VO}_2^+$  cations [20]. It is possible that, along with reactions (IV) and (V), other equilibria exist in these solutions.

### OXIDATION OF ALKYL-SUBSTITUTED PHENOLS INTO *para*-QUINONES

We have developed a number of processes in which HPA- $x'$  solutions serve as effective single-component catalysts for oxidation of alkylphenols of the benzene and naphthalene series into the corresponding *para*-quinones [31–34]. Important products of these reactions are 2,3,5-trimethyl-1,4-benzoquinone (TMQ), which is the key intermediate in the synthesis of vitamin E, and 2-methyl-1,4-naphthoquinone (vitamin K<sub>3</sub>, menadione, MD), which is the precursor of all K-group vitamins [35]. These quinones are obtained by the oxidation of 2,3,6-trimethylphenol ((TMP) [36] and 2-methylnaphthol-1 (2MN1) [32, 37], respectively, according to the following overall reactions:

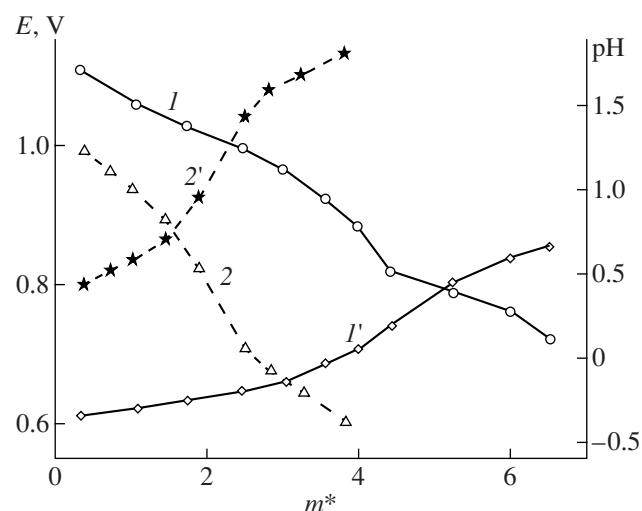


Also of great interest is obtaining 2,6-dialkyl-1,4-benzoquinones, such as 2,6-dimethyl-1,4-benzoquinone (DMQ) and 2,6-di-*tert*-butyl-1,4-benzoquinone (DTQ), from the respective dialkylphenols (DMP, DTP) via the reaction



DMQ is an intermediate in the synthesis of some medicines and physiologically active substances, and DTQ is an intermediate in the synthesis of anti-aging agents, antioxidants [38], and pharmaceutical and perfume formulations [39].

Reactions (VII)–(IX) are carried out in two-phase systems containing a solution of phenol and reaction products in an organic solvent and an aqueous solution of HPA- $x'$ . The products are readily separable from the reduced catalyst by phase sepa-



(1, 2) Redox potential and (1', 2') pH of  $\text{H}_{16}\text{P}_3\text{Mo}_{17}\text{V}_7\text{O}_{84}$  (HPA-7') and  $\text{H}_7\text{PMo}_8\text{V}_4\text{O}_{40}$  (HPA-4) solutions as a function of  $m^*$ : (1, 1') 0.25 M HPA-7' and (2, 2') 0.20 M HPA-4.

ration. Thereafter, the catalyst is regenerated via reaction (II).

The oxidation of the initial phenol into *para*-quinone is a free-radical process and is the result of the abstraction of two protons and four electrons from the phenol molecule [34]. Therefore, when the oxidizer (HPA- $x'$ ) is lacking, intermediate radicals can recombine to form by-products (resins). To avoid this, reactions (VII)–(IX) need to be carried out in the presence of excess HPA- $x'$  [36, 37].

#### Obtaining 2,3,5-Trimethyl-1,4-Benzoquinone

At present, TMQ is commercially synthesized by the catalytic oxidation of TMP with oxygen in the presence of an aqueous solution of  $\text{CuCl}_2$  [40, 41]. This

yields very toxic chloroaromatic compounds. In the presence of HPA- $x'$  solutions, these compounds are not formed, which makes the synthesis of TMQ via reaction (VII) attractive from the environmental standpoint.

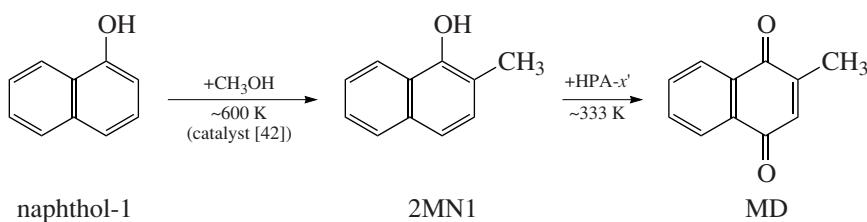
The selectivity ( $S$ ) of reaction (VII) carried out in an  $\text{O}_2$  atmosphere or air at atmospheric pressure depends strongly on the nature of the organic solvent (Table 1). The maximum value of  $S$  (98–99%) is reached in the presence of primary nonbranched  $\text{C}_5\text{--C}_{12}$  alcohols. The maximum productivity ( $600\text{--}800$  (g TMQ)  $1^{-1}$   $\text{h}^{-1}$ ) is reached with modified solutions of HPA- $x'$  with  $x' \geq 6$  [34, 36]. The catalyst retains its high activity and  $S > 98\%$  throughout the prolonged cyclic operation according to reactions (VII) + (II). The productivity and the selectivity of this catalyst far exceed the same parameters of all known ways of obtaining of TMQ.

#### Obtaining 2-Methyl-1,4-Naphthoquinone (MD)

Industrially, MD is obtained by the noncatalytic oxidation of 2-methylnaphthalene with a chromic mixture [35]. The selectivity of this process, which produces a huge quantity of waste (chromium(III) salts and acids), does not exceed 50%. Moreover, 2-methylnaphthalene is poorly available. In Russia, MD is not manufactured.

In the process that we developed for obtaining MD [37], reaction (VIII) is carried out in a two-phase system in the presence of solutions of HPA- $x'$  ( $x' \geq 6$ ) and in the absence of  $\text{O}_2$ . This raises the MD selectivity by 8–10%. The best solvent for this process is trichloroethylene. The addition of acetic acid (HOAc) up to 15 vol % raises  $S$  to ~90% [34].

The oxidation of 2MN1 into MD is the key step of the Vikasib technology, developed at the Institute of Catalysis, Siberian Branch, Russian Academy of Sciences (Scheme 1). This technology is intended for the synthesis of some K-group vitamins, namely, menadione, vikasol (the water-soluble form of vitamin  $\text{K}_3$ ), and menadiol diacetate (vitamin  $\text{K}_4$ ) [33].



Scheme 1.

We obtained vikasol by reacting an aqueous  $\text{NaHSO}_3$  solution with MD [43]; vitamin  $\text{K}_4$  was obtained by the catalytic hydroacetylation of MD in a  $(\text{CH}_3\text{CO})_2\text{O} + \text{HOAc}$  solution [44]. Pilot batches of vikasol and vitamin  $\text{K}_4$  synthesized at the Institute of Catalysis passed biological tests at Siberian farms. These products proved very efficient as additions to

animal feed [45]. Vikasol was certificated for use in livestock farming.

#### Obtaining 2,6-Dialkyl-1,4-Benzoquinones

The main method of the commercial-scale production of DMQ and DTQ is the catalytic oxidation of

**Table 1.** Influence of the primary alcohol chain length on the selectivity of the oxidation of TMP into TMQ in 16 cycles of reaction (VII) in the presence of 0.3 M  $H_{14}P_2Mo_{10}V_8O_{62}$ 

Cycle	Alcohol	Selectivity, %
1	<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	98.6
2	CH <sub>3</sub> OH	64.3*
3	C <sub>2</sub> H <sub>5</sub> OH	73.2*
4	<i>n</i> -C <sub>3</sub> H <sub>7</sub> OH	75.3*
5	<i>n</i> -C <sub>4</sub> H <sub>9</sub> OH	87.1
6	<i>n</i> -C <sub>5</sub> H <sub>11</sub> OH	98.2
7	<i>n</i> -C <sub>6</sub> H <sub>13</sub> OH	98.9
8	<i>n</i> -C <sub>7</sub> H <sub>15</sub> OH	99.5
9	<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	99.5
10	(H <sub>3</sub> C) <sub>3</sub> CCH <sub>2</sub> OH	92.5
11	2-ethylhexanol-1	90.0
12	<i>iso</i> -C <sub>5</sub> H <sub>11</sub> OH	93.5
13	<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	99.6
14	<i>n</i> -C <sub>11</sub> H <sub>23</sub> OH	99.2
15	<i>n</i> -C <sub>12</sub> H <sub>25</sub> OH	99.0
16	<i>n</i> -C <sub>14</sub> H <sub>29</sub> OH	90.5

Note: The reaction was conducted for 15 min at 333 K in an O<sub>2</sub> atmosphere at HPA/TMP = 5 mol/mol; the catalyst was regenerated for 10 min at 433 K and  $P_{O_2}$  = 2 atm [31].

\* Single-phase system.

**Table 2.** Optimum conditions for the oxidation of alkylsubstituted phenols in the presence of HPA- $x'$  solutions via reactions (VII)–(IX) in two-phase systems

Substrate (H <sub>2</sub> Su)	Solvent	Atmosphere	Temperature, K	HPA- $x'$ /H <sub>2</sub> Su molar ratio	Reaction time, h	Product	Selectivity, %	Reference
2,3,6-Trimethylphenol	<i>n</i> -Alcohols C <sub>6</sub> –C <sub>8</sub>	O <sub>2</sub> or air	333	5	0.25	2,3,5-Trimethyl-1,4-benzoquinone	99	[39, 41]
2-Methyl naphthol-1*	Trichloroethylene + 15% AcOH	CO <sub>2</sub>	333	3	0.67	2-Methyl-1,4-naphthaquinone	90	[36, 39, 42]
2,6-Dimethylphenol*	Trichloroethylene + 15% AcOH	CO <sub>2</sub>	333	7.5	1.0	2,6-Dimethyl-1,4-benzoquinone	85	[52, 53]
2,6-Di- <i>tert</i> -butylphenol	Toluene + 30% AcOH	CO <sub>2</sub> or air	353	5	1.5	2,6-Di- <i>tert</i> -butyl-1,4-benzoquinone	83	[52, 53]

\* Gradual introduction of H<sub>2</sub>Su into the HPA- $x'$  solution.

dialkylphenols with oxygen. For example, DMP is oxidized in the presence of copper(II) salts or complexes with nitriles [46] and DTP is oxidized in the presence of vanadium-containing mesoporous molecular sieves [47]. A common disadvantage of these catalysts is their insufficient stability.

In the method developed by us, dialkylphenols are oxidized in a two-phase system via reaction (IX) at 333–353 K [48, 49]. It was demonstrated by the example of DMP that  $S$  depends strongly on the nature of the solvent and the number of vanadium atoms ( $x'$ ) in HPA- $x'$ . The largest value of  $S$  (~85%) was obtained using trichloroethylene and HPA- $x'$  with  $x' \geq 6$  [49].

The optimum solvent for the oxidation of DTP into DTQ is toluene + 30 vol % HOAc [49, 50]. This reaction proceeds more slowly than the oxidation of DMP because of the steric hindrance (screening of the hydroxyl group of phenol by the *tert*-butyl groups).

In the oxidation of DMP, conducting the reaction in the presence of O<sub>2</sub> decreases  $S$  by 30–40%. This is explained by the fact that oxygen favors the formation of free phenoxy radicals. These radicals dimerize readily to form 4,4'-dihydroxydiphenyls, which are then oxidized into 4,4'-diphenoxquinones.

The data listed in Table 2 show that the optimum conditions for the oxidation of different alkylsubstituted phenols in the presence of HPA- $x'$  solutions are different. An important point in the design of these processes is the optimal choice of the organic solvent.

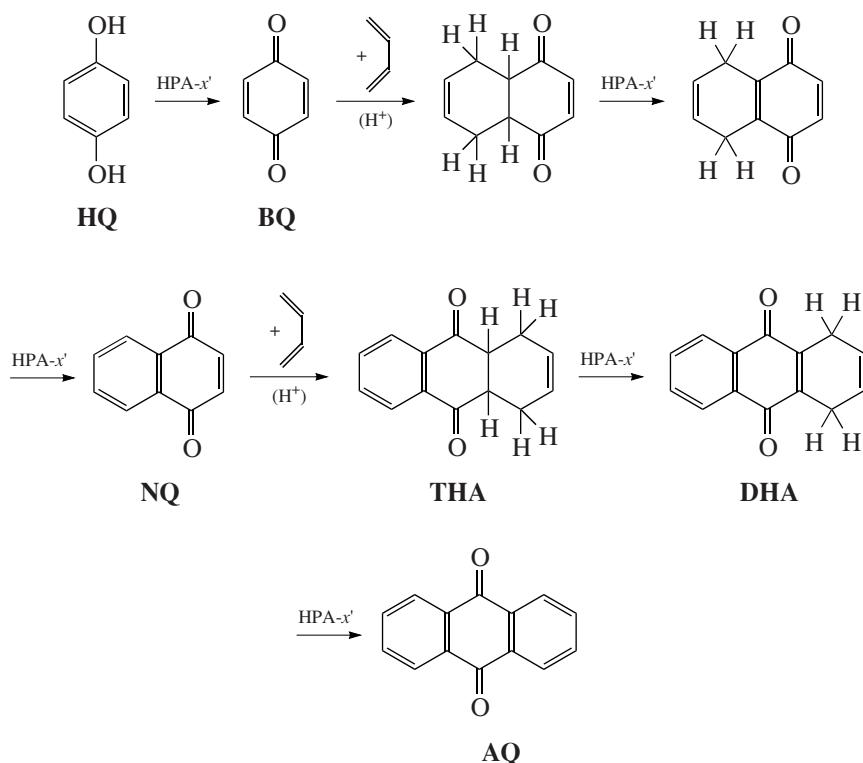
#### USE OF HPA- $x'$ SOLUTIONS AS BIFUNCTIONAL CATALYSTS

Solutions of HPA containing W or Mo are mainly used as acid catalysts for various reactions [4, 51, 52]. In particular, supported W–P HPAs were used earlier as

diene synthesis catalysts in the condensation of 1,4-naphthoquinone with 2,3-dimethyl-1,3-butadiene [53]. A specific feature of solutions of Mo–V–phosphoric HPAs is that they combine acidic and oxidizing properties. Therefore, they can be used as bifunctional catalysts performing consecutive acid-catalyzed and oxidation reactions.

For the first time, we used the bifunctional properties of HPA- $x'$  (HPA- $x$ ) solutions in the synthesis of

anthraquinones [54]. In this synthesis, 1,4-quinone condenses with 1,3-butadiene and this is followed by the oxidation of the resulting adduct. Both steps were combined into a single technological operation. With the use of HPA- $x'$  solutions, it is possible to obtain 9,10-anthraquinone (AQ) from hydroquinone (HQ), *para*-benzoquinone (BQ), or 1,4-naphthaquinone (NQ) (Scheme 2) [54–56].

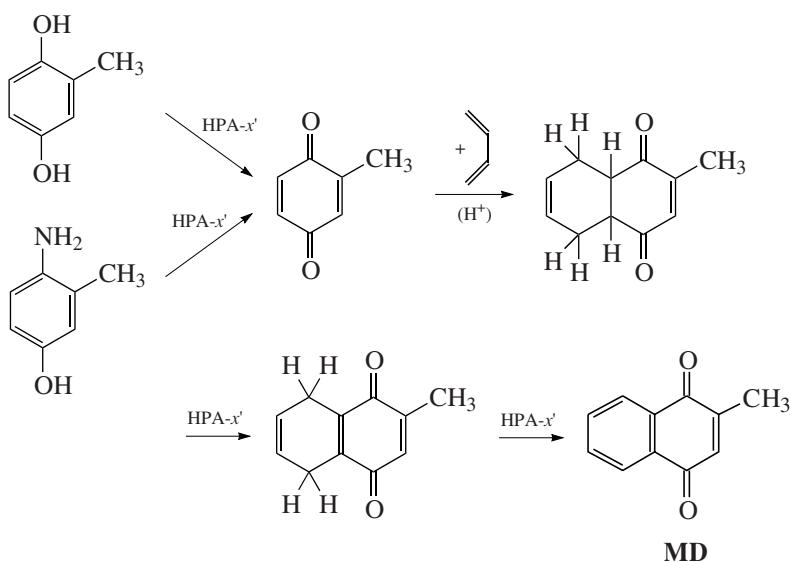


Scheme 2.

It is important that all reactions in Scheme 2 proceed perfectly without an organic solvent upon the introduction of a solid substrate (HQ, BQ, or NQ) into the HPA- $x'$  solution. Stirring a mixture of a substrate and the HPA- $x'$  solution in a 1,3-butadiene atmosphere at  $T < 343$  K and atmospheric pressure results in complete substrate conversion and yields a mixture of AQ and its partially hydrogenated derivatives 1,4,4a,9a-tetrahydro-9,10-anthraquinone (THA) and 1,4-dihydro-9,10-anthraquinone (DHA). For HQ as the starting compound (see Scheme 2), the yield of AQ at atmospheric pressure is 20%; for NQ as the starting compound, the AQ yield is 55%. The products of the reaction (AQ, DHA, and THA) are poorly soluble in water. After the synthesis, they can readily be separated from the aqueous solution of  $\text{H}_m\text{HPA-}x'$  by filtration.

Studies carried out at the Siberian Research Institute for the Wood and Pulp-and-Paper Industries (Bratsk) have shown that the mixture obtained by us (AQ + DHA + THA) is an effective catalyst for wood delignification [50].

Another process in which we utilized the bifunctional properties of HPA- $x'$  solutions is obtaining vitamin K<sub>3</sub> (Scheme 3) from the readily available substrates 2-methylphenol and 2-methylaniline [57, 58]. Upon the introduction of a substrate into an HPA- $x'$  solution in a 1,3-butadiene atmosphere, the substrate oxidizes into 2-methyl-1,4-benzoquinone, which then condenses with 1,3-butadiene, and the resulting adduct oxidizes into MD. The MD yield via this scheme at 313–333 K and atmospheric pressure is ~38–40%.

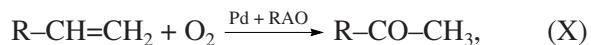


Scheme 3.

By varying the diene and the dienophile, it is possible to considerably widen the range of catalytic processes utilizing the bifunctional properties of the HPA- $x'$  solutions.

#### OXIDATION OF C<sub>2</sub>–C<sub>4</sub> OLEFINS

The catalytic oxidation of lower olefins with oxygen is generally described by the equation

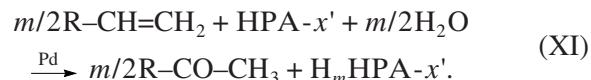


where RAO is a reversibly acting oxidizer and R = H, CH<sub>3</sub>, or C<sub>2</sub>H<sub>5</sub>. The product of the reaction is acaldehyde for R = H, acetone for R = CH<sub>3</sub>, and methyl ethyl ketone (MEK) for R = C<sub>2</sub>H<sub>5</sub>. Wacker Chemie AG once suggested using an aqueous solution of palladium and copper chlorides as the catalyst for reaction (X) [59–61]. However, the use of CuCl<sub>2</sub> as the RAO leads to the formation of harmful organochlorine compounds as by-products, whose amount is particularly large (up to 20%) in the oxidation of *n*-butylenes into MEK [62].

The use of aqueous HPA solutions as RAO, which are free of Cl<sup>–</sup> ions, allowed the problem of the formation of organochlorine compounds to be completely eliminated.

The oxidation of olefins in the presence of two-component catalytic systems (Pd complex + HPA- $x'$ ), like the oxidation of phenols in the presence of an HPA- $x'$  solution as a one-component catalyst, is carried out in

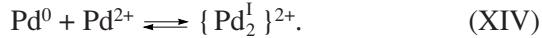
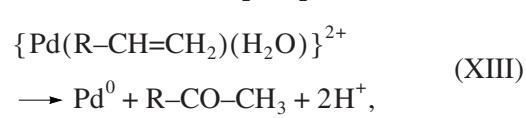
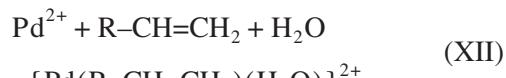
two steps. The first step is the oxidation of R-CH=CH<sub>2</sub> (reaction (XI)), during which the catalyst is reduced:



The products of reaction (XI) in the form of an aqueous azeotrope are stripped off the catalyst, which is then regenerated with oxygen (air) via reaction (II) [20].

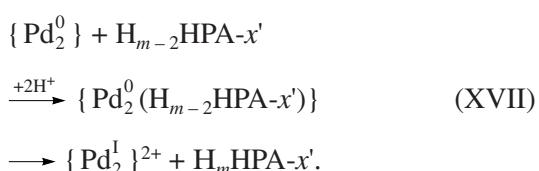
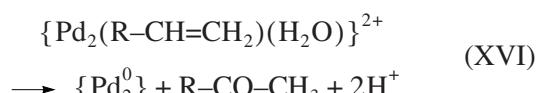
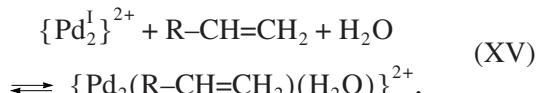
Our investigations on the use of HPA- $x$  solutions in oxidation catalysis began in the 1970s with the oxidation of ethylene with oxygen into acetaldehyde [1, 2, 63] and the oxidation of *n*-butylenes into MEK [2, 64, 65]. Systems containing Pd and Keggin HPA- $x$  solutions were used as catalysts for process (X) at that time. Even though this choice now seems to be nonoptimal, it attracted our attention by being environmentally friendly owing to the absence of organochlorine compounds in the reaction products.

Investigation of the mechanism of reaction (XI) [20, 66, 67] lead us to conclude that, in the absence of Cl<sup>–</sup> ions, Pd(II) is initially reduced rapidly by olefins in the HPA- $x'$  solution to form dimeric Pd(I) complexes:



In the presence of these complexes, further olefin oxidation proceeds in the steady-state region of reaction (XI) at a constant rate via route (XV)–(XVII) up to

almost complete HPA- $x'$  reduction. The rate-limiting step is reaction (XVII).



The selectivity of ethylene oxidation into acetaldehyde and of propylene oxidation into acetone in the presence of Pd + HPA- $x'$  exceeds 99%, and the selectivity of butene-1 oxidation into MEK is 98% [20].

In recent years, we have developed, in detail, a commercial process for the liquid-phase oxidation of *n*-butylenes into MEK [19, 28–30]:



MEK is an excellent solvent and lubricant dewaxer. The existing technologies of its synthesis are multistep processes producing large amounts of waste [68]. In Russia, MEK is not manufactured.

We have optimized the conditions for both steps of process (XVIII) [20, 30]. A pilot plant has recently been created at OOO Sintez-Inzhiniring (Dzerzhinsk) in order to refine this technology. Trial operation of this plant has demonstrated that the modified HPA- $x'$  solutions are sufficiently stable.

Catalytic oxidation processes using solutions of Mo–V-phosphoric HPAs have not been commercialized as yet. However, the high stability of the modified HPA- $x'$  solutions suggests that they can be used to develop a variety of important catalytic oxidation processes for basic and fine organic synthesis.

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