ELSEVIER

Journal of Molecular Catalysis A: Chemical 114 (1996) 151–160

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Heteropoly acids as oxidation catalysts in synthesis of K-vitamins

K.I. Matveev *, V.F. Odyakov, E.G. Zhizhina

Boreskov Institute of Catalysis, 630090 Novosibirsk, Russia

Abstract

Mo–V–phosphoric heteropoly acids of the Keggin structure $H_{3+n}PMo_{12-n}V_nO_{40}$ (HPA-*n*) and their acidic salts were found to be efficient catalysts for 2-methyl-1-naphthol (MN) oxidation by dioxygen to 2-methyl-1,4-naphthoquinone (menadione, or vitamin K_3). The reaction occurs in two steps: (1) HPA-*n* reduction by MN followed by the product isolation; (2) HPA-*n* regeneration by dioxygen. For reaction MN + HPA-*n*, carried out in a two-phase 'water + organic' solvent system, it has been studied how the HPA-*n* composition and reaction conditions affect the HPA-*n* selectivity and activity. The reaction mechanism and methods of increasing the catalyst selectivity are suggested. The reaction has been used in scope of a new environmentally harmless technology 'Vikasib' producing the K-group vitamins.

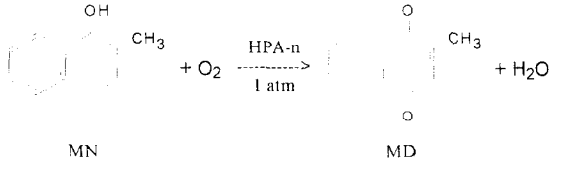
Keywords: Oxidation catalysis; Mo–V–phosphoric heteropoly acids; K-vitamins; Synthesis; Mechanism; Selectivity

1. Introduction

We have already successfully used Mo–V–phosphoric heteropoly acids $H_{3+n}PMo_{12-n}V_nO_{40}$ (HPA-*n*) and their acidic salts as catalysts to oxidize methylphenols of benzene and naphthalene family to 1,4-quinones [1]. The methylated 1,4-quinones of the benzene family proved to play the key role in the synthesis of vitamin E [2,3]. At the same time vitamin K_3, 2-methyl-1,4-naphthoquinone (menadione, MD), is the starting reagent in the synthesis of all vitamins of the K-group [4].

Almost all MD producing technologies use a hardly accessible 2-methylnaphthalene as a raw material. It is noncatalytically oxidized by chromium (VI) salts to MD [5]. The 'Vikasib' technology [6] is an alternative method for MD production. Certain catalytic reactions can be used to overcome the disadvantages of the other known technologies producing MD and K vitamins.

In 'Vikasib' technology, easily available naphthol-1 is the raw material. Eq. (1), which is the 2-methyl-1-naphthol (MN) oxidation by dioxygen to MD in the presence of HPA-*n* solutions, is the key stage [6,7]. Eq. (1) is a sum of two complex processes, Eq. (2) and Eq. (3):



(1)

* Corresponding author.

PII S1381-1169(96)00313-5

$$\tfrac{1}{4}m\ \mathrm{MN} + \tfrac{1}{4}m\ \mathrm{H_2O} + \mathrm{HPA}\text{-}n \xrightarrow[35-50^\circ\mathrm{C}]{} \tfrac{1}{4}m\ \mathrm{MD} + \mathrm{H}_m\mathrm{HPA}\text{-}n \quad (2)$$

$$\mathrm{H}_m\mathrm{HPA} + \tfrac{1}{4}m\ \mathrm{O_2} \xrightarrow[100^\circ\mathrm{C}]{} \mathrm{HPA} + \tfrac{1}{4}m\ \mathrm{H_2O} \quad (3)$$

Actually, it is reasonable to perform Eq. (1) in two steps. At step Eq. (2) substrate MN is oxidized by the HPA-*n* solution to MD without dioxygen. After reaction products are separated, H_mHPA-*n* (reduced HPA-*n* species) produced is oxidized by dioxygen at 100°C (step Eq. (3)), and thus HPA-*n* is recovered. In this case no further MD oxidation occurs. The oxidized HPA-*n* may be repeatedly used in Eq. (2).

In the present paper we discuss a possible mechanism of Eq. (2) and how to optimize the composition of HPA-*n* used as a catalyst for Eq. (1) in order to attain the highest selectivity.

2. Experimental

Heteropolyacids $H_{3+n}PMo_{12-n}V_nO_{40}$ (HPA-*n*, $n = 1$–4) and their acidic salts, used as catalysts, were synthesized from H_3PO_4, MoO_3 and V_2O_5 by procedures described in [8].

In order to study Eq. (2), a synthetic 2-methyl-1-naphthol (MN) of no less than 95% purity was used. The main impurity was 2,4-dimethyl-1-naphthol, which was also oxidized to MD during the reaction.

Eq. (2) was performed in a 100 ml reactor in CO_2 by means of unsteady-state catalysis in the two-phase water + organic solvent (benzene, hexane, etc.) system. The substrate (MN) and reaction product (MD) resided in the organic phase, while the catalyst (HPA-*n*) stayed in water. Eq. (2) proceeded over the interface under intensive agitation at 35–50°C. After the reaction phases were separated. To prevent the losses of MD and catalyst, water phase was washed by the organic solvent, and the organic phase was washed by water. The washing solutions were respectively added to the catalyst and organic solvent. The organic solvent was distilled and returned to the reaction. The rest MD amount was determined as follows. MD was quantitatively reduced by the zinc powder excess in the presence of small quantities of iodine (I_2 was reduced to I^-). Thus produced menadiol was then titrated by the 0.1 N diiodine solution in the acetate buffer [9]. The water phase containing H_mHPA-*n* was evaporated to its initial volume, while HPA-*n* recovered in Eq. (3).

Reaction products (except for nonvolatile resins) were identified by the GLC-method using chromatograph Tsvet-500 with a flame-ionization detector and temperature programming from 150 to 200°C. A 1 m column (i.d. 3 mm) was filled with 5% SE-30 on NW-D-4 CS (fraction 0.16–0.20 mm); helium served as a carrier gas (40 ml/min).

The catalyst selectivity in Eq. (2) was estimated by the balance experiments. After Eq. (2) performance, phase separation and solvent distillation, MD was isolated from resins by a steam distillation. Then MD was extracted by chloroform from the aqueous condensate. The extract was dried at 30–40°C, and thus obtained pure MD was weighted. The resin residue was extracted by chloroform. Then chloroform was evaporated, and thus obtained resin was weighted to determine its yield.

The HPA-*n* selectivity in Eq. (2) was estimated as a ratio of actual MD yield to that expected theoretically. Here we observed some disbalance, as the bright-colored water-soluble resin and phthalic acid (see below), that can not be extracted by chloroform, remain in the aqueous solution. The rates of Eq. (2) for various HPA-*n* and their salts were determined by the time of half-conversion of MN ($\tau_{1/2}$). In the reaction course, the organic phase samples were taken in 1, 2, 3, 4, 5, 10, 15, 20, 25 min and then analyzed using chromatography.

The NMR spectra (^{31}P, ^{51}V) of the HPA-*n* solutions were recorded using a high-resolution NMR spectrometer 'Bruker' (MSL-400), with H_3PO_4 or $VOCl_3$ as references.

The oxidation potentials, *E*, of HPA-*n* and their salts were measured by digital ionometer

Table 1
Dependence of catalyst selectivity (s) in Eq. (2) and ratio $g_{MD}:g_{res}$ on HPA-n composition

HPA-n	s (%)	$g_{MD}:g_{res}$
$H_4PMo_{11}VO_{40}$	81.5	6.9
$H_5PMo_{10}V_2O_{40}$	89	7.9
$H_6PMo_9V_3O_{40}$	85	6.1
$H_7PMo_8V_4O_{40}$	82	4.7
$Fe^{III}_{0.6}H_{4.2}PMo_9V_3O_{40}$	75	5.1
$Cr^{III}_{0.6}H_{4.2}PMo_9V_3O_{40}$	70.5	3.6
$Mn_{0.9}H_{4.2}PMo_9V_3O_{40}$	71	3.8
$Zn_{0.9}H_{4.2}PMo_9V_3O_{40}$	70.5	3.7
$Cu_{0.9}H_{4.2}PMo_9V_3O_{40}$	70	3.5
$Co_{0.9}H_{4.2}PMo_9V_3O_{40}$	70.5	3.8
$Mg_{0.9}H_{4.2}PMo_9V_3O_{40}$	70.5	3.8
$Na_{1.8}H_{4.2}PMo_9V_3O_{40}$	71	3.9

Conditions: $t = 50°C$, [HPA-n] = 0.2 M, [HPA-n]:[MN] = 4.

I-130 at room temperature. Platinum (EPV-1) and saturated silver chloride electrodes were used as indicating and reference electrodes, respectively. E values referred to the normal hydrogen electrode (NHE) were presented for HPA-n reduction by 0.5 e, HPA-n being assumed as a single electron oxidant.

3. Results and discussion

The optimum temperatures for Eq. (2) range from 35 to 50°C. At higher temperatures the relative rate of side reactions grows, while at lower temperatures the main reaction rate decreases.

In order to increase the catalyst selectivity in Eq. (2), it was necessary to find parameters providing a higher rate of the main reaction and lower rates of the side reactions producing resins. The total rate of all MN conversions, $\sum W_i$ is proportional to the rate of Eq. (2), W_2, and to catalyst selectivity s through equation $\sum W_i = W_2(1/s - 1)$. We believe that it is possible to inhibit some side reactions optimizing the catalyst composition and using the oxidizing properties of the catalyst. Those side reactions that do not depend on the catalyst composition we can avoid varying reaction conditions.

Experimental results, shown in Tables 1 and 2 and Fig. 1 confirmed our expectations. The rate of Eq. (2) is strongly dependent on some parameters, the HPA-n molecule composition and reaction conditions being among them.

Separating Eq. (2) and Eq. (3) steps, we improved the catalyst selectivity in Eq. (2) from ca. 50% to ca. 75%.

For HPA-n with $1 \leq n \leq 4$ we have studied how the number of vanadium atoms, n, in the HPA-n molecules affects the catalyst activity and selectivity. As n increases, the MN half-conversion time decreases, and the HPA-n activity grows (Fig. 1). The decrease of $\tau_{1/2}$ correlates with the growing oxidation potential E. For HPA-1, $\tau_{1/2}$ was not attained, since less than half of MN was oxidized even at [HPA-1]:[MN] = 4. The reason is a fast decrease of the HPA-n oxidation potential, as it is being reduced (Fig. 2).

We also studied how the catalyst selectivity in Eq. (2) and ratio $g_{MD}:g_{res}$ (g_{MD} and g_{res} are the menadione and resin weights, respectively) depend on the HPA-n composition (Table 1). The data were obtained in the balance experiments.

Table 1 and Fig. 1 show that among all HPA-n, HPA-2 has the maximum selectivity, whereas the maximum reaction rate W_2 occurs for HPA-4. The MN oxidation rate changes antibately with the selectivity of catalysts in the

Table 2
Influence of the out-sphere cations on oxidation potentials of HPA-3 salts ([HPA-3] = 0.2 M, in its salts two H^+ are substituted)

	HPA-3	MgHPA-3	CoHPA-3	MnHPA-3	Na_2HPA-3	$Fe_{0.67}$HPA-3
E (V) [a]	0.760	0.725	0.730	0.728	0.725	0.730

[a] Relative to NHE.

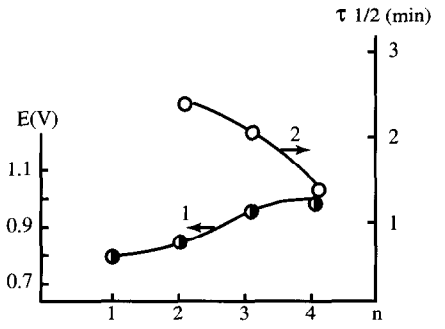


Fig. 1. Oxidation potentials, E, and 2-methyl-1-naphthol half-conversion time, $\tau_{1/2}$, versus the number of vanadium atoms in HPA-n, n, at 25°C. For E given relative to NHE [HPA-n] = 0.2 M. For $\tau_{1/2}$ – [HPA-n] = 0.1 M, [HPA-n]:[MN] = 4.

series: HPA-2 < HPA-3 < HPA-4. As the optimum W_2 and s occur at different n, the ΣW_i and W_2 changes are not in proportion, when n changes.

So the best catalysts for Eq. (2) are those HPA-n, whose oxidation potentials are not very high. According to our data, the oxidation potentials of HPA-3 and HPA-4 (for HPA reduction degrees ranging within $1 < m < 2$) are 0.82 and 0.87 V, respectively (Fig. 2). They are comparable with that of HPA-2 at $m = 0.5$ e^- (Fig. 1), which has a higher selectivity in MN oxidation (Table 1).

As follows from the stoichiometry of Eq. (2); each MN molecule gives 4 electrons to HPA-n, when MN is oxidized to MD. Since the HPA-2 molecule can accept no more than 2 electrons from MN, several HPA-2 molecules should participate in the reaction. This is true also for the HPA-3 and for HPA-1 molecules. Later we proposed that all HPA-n reacting with MN are the associates of several V-containing species.

We have studied the role the outer coordination sphere composition for the acidic HPA-3 salts with various metal cations. The degree of cation substitution for H^+ was 1.8 (Table 1). The selectivity of HPA-3 salts is lower than that of HPA-3 itself. It is almost independent of the outer sphere cation nature. It is 70–71% for most acidic salts. $Fe^{III}_{0.6}H_{4.2}PMo_9V_3O_{40}$ is the only exception. It is the most selective HPA-n salt, providing a higher MN oxidation rate than other HPA-3 salts do. This phenomenon seems to relate to the oxidative properties of Fe^{3+}, which oxidizes the intermediate naphthoxyl radicals, thus being reduced to Fe^{2+}. So the catalyst activity and selectivity in Eq. (2) is determined not only by their oxidation potential but also by their acidity and the outer sphere cations participation in the electron transfer from the oxidized substrate to HPA-n.

The substitution of metal cations for H^+ in HPA-n decreases the solution acidity and its oxidation potential E. Fig. 3 presents E as a function of m for the acidic Mg^{2+} salts of HPA-n ($n = 1$–4) and for HPA-3. The acidic HPA-n salts with various cations but the same H^+ substitution degree have the similar E values (Table 2). The pH values of various HPA-3 salt solutions are approximately the same and equal to 1.2 at a H^+ substitution degree of 1.8 (Table 1).

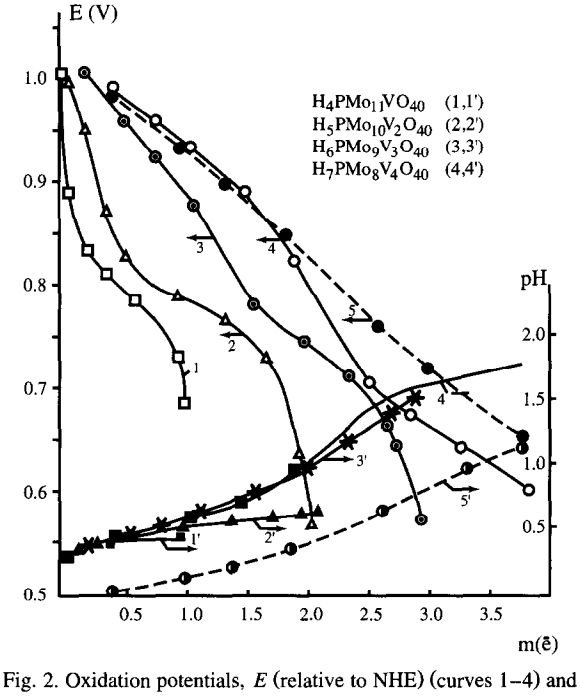
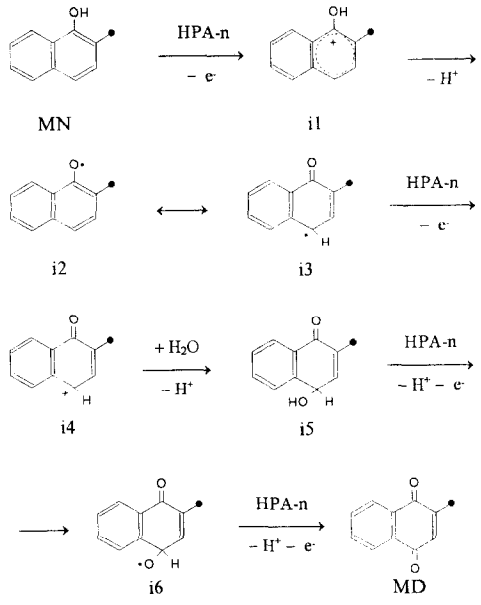


Fig. 2. Oxidation potentials, E (relative to NHE) (curves 1–4) and pH (curves 1′–4′) versus HPA-n reduction degree, m, for aqueous 0.2 M HPA-n solutions at room temperature. Curves 5,5′ are given for 0.1 M HPA-4 in aqueous 50% HOAc.

Decreasing the MN concentration in Eq. (2), we obtained a higher MD yield and a lower amount of resins. The organic MN solution was gradually added to the aqueous HPA-*n* solution, as MN was being oxidized. The catalyst selectivity in Eq. (2) also rose, as molar ratio [HPA-*n*]:[MN] grew. The optimum molar ratio was found to lie within $3 < [\text{HPA-}n]:[\text{MN}] < 4$. As it grew higher, the selectivity increased insignificantly, but the reaction mixture volume enlarged sharply.

The main path of Eq. (2) (see Scheme 1) is one of the probable paths in the oxidation processes catalyzed by heteropoly compounds and summarized in the excellent review by Hill [10], which to a high extent stimulated the present study.

The reaction starts as the MN + HPA-*n* complex forms over the interface. (Here HPA-*n* is an associate of several V-containing species.) Similar complexes were reported in a number of papers concerning the oxidation of various phenols [11,12] and terpenes [13]. In the MN + HPA-*n* system several single-electron transfers occur, which alternate with the proton split-off, and reaction of carbocation i4 with the solvent. Finally, reaction product MD splits off from the reduced HPA-*n*.



Scheme 1.

This mechanism assumes that HPA-*n*, similar to the VO_2-ion, is a single-electron oxidant [14,15]. According to Scheme 1, the MN oxidation passes through a series of consequent single-electron transfers with proton elimination. The complete MN oxidation to MD requires 4 electron transfers from MN to HPA-*n*. The more electrons HPA-*n* can take from MN, the less probable are the cleavage of the i1–i6 intermediates from HPA-*n* and their resin producing reactions.

Dimers, trimers, etc., of MN and MD (C_{22}, C_{33}, C_{44}, etc.), i.e. resins, are assumed to be the side products of Eq. (2). Most of them (DN, DN_2) seem to result from intermediate radicals i3, which then recombine yielding dioxydinaphthyl (DN) by Eq. (5). The similar reactions of the oxidative phenol dimerization are well known in the organic chemistry [16]. According

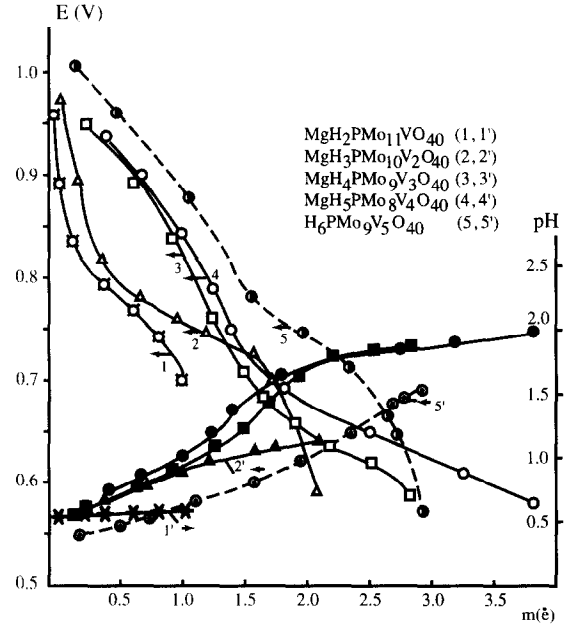
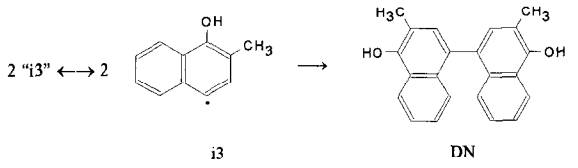


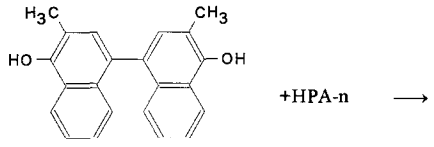
Fig. 3. Oxidation potentials, *E* (relative to NHE) (curves 1–4) and pH (curves 1′–4′) versus reduction degree of Mg salts of HPA-*n*, *m*, for aqueous 0.2 M Mg salt solutions at room temperature. Curves 5,5′ are given for aqueous 0.2 M HPA-3.

to [17], dimer DN is oxidized to dinaphthoquinone DN_2 by Eq. (6).



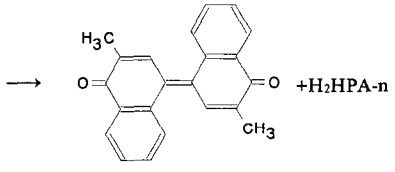
i3 DN

(5)



DN

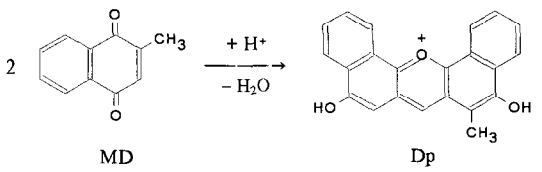
(6)



DN_2

Eq. (5) and Eq. (6) are the branches of the main path of Scheme 1. Their rates may decrease, as the strength of the bond of i3 and i4 with HPA-*n* increases. The bond strength depends on the HPA-*n* composition, which may be varied. The information about the HPA-*n* composition and properties during Eq. (2) are given below.

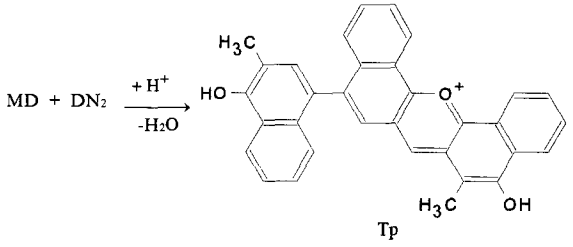
The products of further MD conversion proved to be the side products of Eq. (2). MD (like other methylquinones) is affected by strong acid dimerizations by Eq. (7), thus producing water-soluble bright-purple dinaphthopyrylium salt Dp [18]. All HPA-*n* are the strong Broensted acids and catalyze various acidic reactions [19,20], including Eq. (7).



MD Dp

(7)

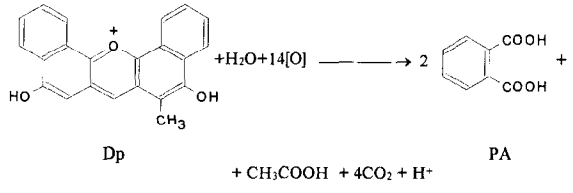
DN_2 can enter the similar Eq. (8).



Tp

(8)

Dp and Tp seem to be oxidized during Eq. (3) by dioxygen to phthalic acid (PA), which little by little accumulates in the solution, Crystallized PA was identified by the melting point, 234°C (according to [21]), and IR spectra.



Dp PA

+ CH_3COOH + $4CO_2$ + H^+

(9)

We can reduce the rates of Eq. (7)–Eq. (9), decreasing the acidity or changing the HPA-*n* composition or substituting some H^+ of HPA-*n* by metal ions.

Using the NMR (^{31}P, ^{51}V) spectra (Fig. 4) we determined the composition of various oxidized HPA-*n* species in the solution. We have found that in the aqueous solution all HPA-*n*

(except for HPA-1) are not individual compounds. An HPA-*n* appears to be a mixture of manifold particles, that are in mutual fast equilibria involving the solvent [22,23]. With regard to chemical thermodynamics such equilibria allow to consider this mixture as a single compound (HPA-*n*) where properties of numerous particles are averaged statistically. So the HPA-*n* selectivity in Eq. (2) also is one of such properties. The highest selectivity (100%) is not attainable because of the complex composition of the catalyst molecules.

When the HPA-*n* molecules are reduced by MN, we fail to use NMR, since reduced H_mHPA-*n* molecules containing V(IV) are paramagnetic. Therefore, reduction causes a significant broadening of all spectral lines.

As all the properties of HPA-*n* solutions and its ability to be reoxidized conserve the HPA-*n* redox reactions, all the equilibria between the oxidized and reduced HPA species also conserve. The simultaneous presence of oxidized and reduced species increases sharply the number of equilibria in the solution [22,23]. Therefore, it is possible to describe all HPA-*n* properties in the solution only in terms of chemical thermodynamics and kinetics.

The equilibrium between dissimilar particles in the solution means the equality of their free energies and oxidation potentials E. So we used E and its derivative dE/dm to estimate the qualitative alterations in the catalyst composition during Eq. (2). Note that the equality of particle potentials does not at all mean the equality of their reactivities towards MN yet.

An idea that HPA-*n* selectivity in alkylphenol

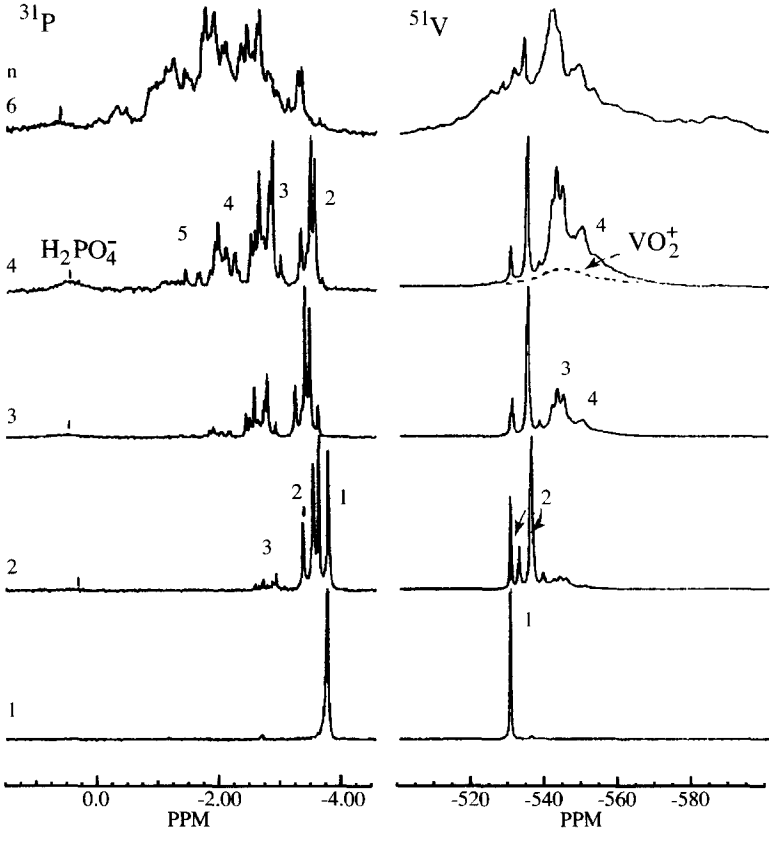


Fig. 4. NMR spectra (^{51}V, ^{31}P) of HPA-*n* 0.2 M solutions ($H_{3-n}PMo_{12-n}V_nO_{40}$), n = 1–4, 6, at room temperature. (A series of lines for individual HPA-*n* are marked with figures.) pH values of HPA-*n* solutions are: 0.31 for n = 1, 0.34 for n = 2, 0.40 for n = 3, 0.44 for n = 4, 0.53 for n = 6. The positions of our spectral lines for HPA-*n* with n = 1 and 2 agree with those of corresponding lines in [22].

oxidation depends on the redox-potential had been expressed before [12]. This seems to be beyond doubt. But all existing hypotheses ignore the difference of particles composing the HPA-*n* solutions. With this regard it is necessary to revise the ways improving the selectivity of HPA-*n* oxidation catalysts. We also consider peculiarities of phenols. In the oxidation reactions involving these compounds, the catalyst must pick up not one, but many electrons from the substrate molecule, otherwise the oxidation will be non-selective. But the single stage multi-electron transfers prove to be thermodynamically forbidden. This is why our reaction can be only a multi-step conversion, each step being accompanied by the single-electron transfer. Moreover, conversion can never be accompanied by the charge accumulation on the particles. The substrate must not loose its bonding to the catalyst in the course of steps passing. Otherwise our reaction will be non-selective. All these requirements are taken into account in Scheme 1 and are amended by the approximate rating presented below.

The most reactive particles towards various substrates are the VO_2^+ ions [14,15] (see also [3]). These ions are produced, when HPA-*n* with a high vanadium content ($n > 2$) dissociates [8,24]. Then the VO_2^+-ions insert into the outer coordination sphere of the same defect HPA-*n* molecule:

$$H_{3+n}PMo_{12-n}V_nO_{40} + H_2O \overset{H^+}{\rightleftarrows} (VO_2)H_{5+n}PMo_{12-n}V_{n-1}O_{39} \quad (10)$$

The concentrations of quasi-free VO_2^+ in the HPA-*n* solutions vary along with *n* and solution dilution [8]. This explains the increase in the activity and oxidation potential of HPA-*n* in the series $1 \leq n \leq 4$ (Figs. 1 and 2). The catalyst selectivity in Eq. (2) varies in a far more complex manner, and the most selective catalyst is HPA-2.

A free VO_2^+ is a strong single-electron oxidant [25]. So, its presence increases the probability of the single-electron MN oxidation producing naphthoxyl radicals i3 (Scheme 1) producing DN after their recombination. This in-

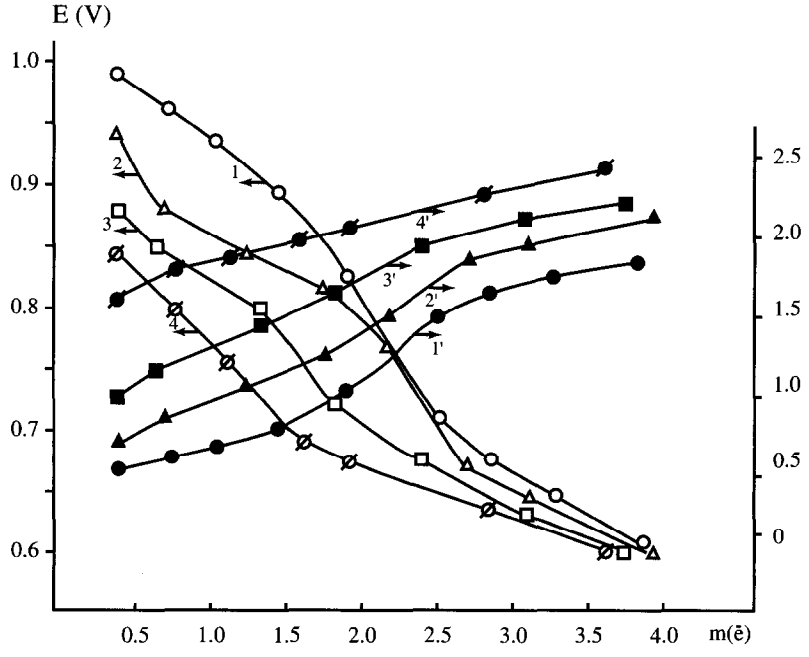


Fig. 5. Oxidation potentials, *E* (relative to NHE) (curves 1–4) and pH (curves 1′–4′) versus reduction degree, *m*, for HPA-4 aqueous solutions of different concentrations at room temperature: 1,1′ – 0.2 M; 2,2′ – 0.1 M; 3,3′ – 0.05 M; 4,4′ – 0.01 M.

creases the rate of side Eq. (5) and decreases the catalyst selectivity in Eq. (2).

According to Scheme 1, a further increase in the catalyst selectivity in Eq. (2) may be attained by strengthening its complexes with MN and produced radicals i1–i6. We may do this by increasing the number of vanadium atoms in the average statistical catalyst particle. This number (n_0) may be estimated on the condition that the catalyst oxidation potential exceeds that for i1–i6 (E_{ip}) in all reaction steps. E_{ip} values are unknown. Only for i2 ↔ i3 $E_{i2 \leftrightarrow i3}$ may be estimated on the basis of Refs. [26,27]. Thus, the oxidation potential of the $1\text{-}C_{10}H_7O^{\cdot}/1\text{-}C_{10}H_7O^{-}$ couple is 0.402 V in the dimethylsulfoxide solution [27]. As for phenols, CH_3 group in position 2 decreases the oxidation potential of the phenoxyl/phenolate couple by 0.075 V. So $E_{i2 \leftrightarrow i3} = 0.402 - 0.075 = 0.327$ V. Assuming that the oxidation potential of the i6/MD couple lies between $E_{i2 \leftrightarrow i3}$ and $E_{MD/MH} = 0.412$ V [28], where MH is 2-methyl-1,4-naphthohydroquinone, we obtain $E_{i6/MD} = 0.5 \cdot (E_{i2} + E_{MD/MH}) = 0.5 \cdot (0.327 + 0.412) = 0.370$ V.

As the oxidative potential of HPA-*n* slowly decreases with the growing *m*, the catalysts of Eq. (2) most likely react with substrate MN. Moreover, they react as associates consisting of several statistically averaged particles. The strengthening of such associates should provide a higher selectivity of the catalysts.

The solvent is responsible for all equilibria of the HPA-*n* composition redistribution in the solution. So, beside the HPA-*n* composition, the solvent nature and HPA-*n* concentration also affect the equilibrium composition of particles. Fig. 5 shows the influence of the HPA-4 concentration on *E* versus *m*. Actually, *E* dependence on *m* changes, as the solvent nature varies (compare curve 2 of Fig. 5 with curve 5 of Fig. 2). Comparison proves that both solvent nature and HPA-*n* concentration affect the mean statistic particle composition of reduced HPA-*n*. The same effect for the oxidized HPA-*n* species was established in [24]. Thus, changing the solvent we most likely can influence the HPA-*n* selectivity.

The solutions of Mo–V–phosphoric heteropoly acids are also good catalysts for oxidizing the substituted phenols to 1,4-quinones [1] as well as to 1,4-quinols and their derivatives [29,30]. However, the required catalyst selectivity is attained only when positions 2 and 6 of the phenol molecule are occupied by the alkyl substituents R ($R = CH_3$ [1,3], $(CH_3)_3C$ [29,30]). This is explained by a high reactivity of the radical states in the above positions, also complying with Scheme 1.

References

[1] K.I. Matveev, E.G. Zhizhina and V.F. Odyakov, in: EUROPACAT-1 (1st Eur. Congr. on Catal.), Book of Abstracts, Vol. 1, ENSCM, Montpellier (1993) p. 355.

[2] G.S. Chernikova, N.G. Baranova, U.M. Azizov and I.B. Afanas'ev, Khim. Farm. Zh. 22 (1988) 1244.

[3] O.A. Kholdeeva, A.V. Golovin, R.I. Maksimovskaya and I.V. Kozhevnikov, J. Mol. Catal. 75 (1992) 235.

[4] V.M. Berezovskii, Khimiya Vitaminov, 2nd Ed. (Pishchevaya promyshlennost', Moscow, 1973) p. 286.

[5] L.O. Shnaidman, Proizvodstvo Vitaminov, 2nd Ed. (Pishchevaya promyshlennost', Moscow, 1973) p. 335.

[6] K.I. Matveer, E.G. Zhizhima, V.F. Odyakov, N.S. Kotsarenko and V.P. Shmachkova, in: II Conf. Modern Trends in Chem. Kinet. and Catal., Novosibirsk, Russia, November 21–24 (1995), Abstracts, Part II (1), p. 293; React. Kinet. Catal. Lett. 57 (1996) 182.

[7] K.I. Matveev, A.P. Krysin, T.F. Titova, B.M. Khlebnikov, V.F. Odyakov, T.G. Egorova, E.G. Zhizhina and V.N. Parmon, Rus. Pat. 2022958, 1994, Byull. Izobret. 21 (1994).

[8] V.F. Odyakov, E.G. Zhizhina, R.J. Maksimovskaya and K.I. Maiveev, Kinet. Katal. 36 (1995) 795.

[9] V.F. Odyakov, E.G. Zhizhina and K.I. Matveev, Khim. Farm. Zh. 30 (1996) 50.

[10] C.L. Hill and C.M. Prosser-McCartha, Coord. Chem. Rev. 143 (1995) 407.

[11] R. Neumann and M. Lissel, J. Org. Chem. 54 (1989) 4607.

[12] M. Lissel, H. Jansen in de Wal and R. Neumann, Tetrahedron Lett. 33 (1992) 1795.

[13] R. Neumann and M. Levin, J. Am. Chem. Soc. 114 (1992) 7278.

[14] T.A. Gorodetskaya, I.V. Kozhevnikov, K.I. Matveev, V.N. Sidel'nikov and R.I. Maksimovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 33 (1984) 929.

[15] E.G. Zhizhina, L.I. Kuznetsova and K.I. Matveev, React. Kinet. Catal. Lett. 31 (1986) 113.

[16] K.-F. Wedemeyer, in: Houben-Weil Methoden der Organischc Chemie, 4 Auflage, Bd. VI/Ic, Phenolc, Teil 2 (G. Thieme: Stuttgart, 1976) p. 1121.

[17] R. Lesser, A. Glaser and G. Aczel, Liebigs Ann. Chem. 402 (1913) 1.
[18] H.J. Kallmayer, Arch. Pharm. (Weinheim) 305 (1972) 776.
[19] I.V. Kozhevnikov and K.I. Matveev, Usp. Khim. 51 (1982) 1875; Appl. Catal. 5 (1983) 535.
[20] I.V. Kozhevnikov, Usp. Khim. 62 (1993) 510.
[21] Dictionary of Organic Compounds, 5th Ed., Vol. 1 (Chapman&Hall, New York, 1982) p. 532.
[22] L. Pettersson, I. Andersson, A. Selling and J.H. Grate, Inorg. Chem. 33 (1994) 982.
[23] L. Pettersson, in: Polyoxometalates, M.T. Pope and A. Mueller (Eds.) (Kluwer Acad. Publ., Dordrecht, 1994) p. 27.
[24] O.A. Kholdeeva and R.I. Maksimovskaya, Russ. J. Inorg. Chem. 37 (1992) 1349.
[25] Freeman, in: Organic Syntheses by Oxidation with Metal Complexes, W.J. Mijs and C.R.H.I. de Jonge (Eds.) (Plenum, New York, 1986) p. 8.
[26] J. Lind, X. Shen, T.E. Eriksen and G. Merenyi, J. Am. Chem. Soc. 112 (1990) 479.
[27] F.G. Bordwell and J.-P. Cheng, J. Am. Chem. Soc. 113 (1991) 1736.
[28] O.S. Ksenzhek and S.A. Petrova, Elektrokhimicheskiesvoistva Obratimykh Biologicheskikh Redokssistern (Moscow, 1986) p. 102.
[29] T.F. Titova, A.P. Krysin, E.G. Zhizhina and K.I. Matveev, Zh. Organ. Khim. 27 (1990) 1321.
[30] T.F. Titova, K.I. Matveev, V.F. Odyakov and A.P. Krysin, Zh. Prikl. Khim. 63 (1990) 1761.