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Feature Article

Catalytic way of transforming 2,3-dimethylphenol to *para*-quinone with the use of vanadium-containing heteropoly acids

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ABSTRACT

2,3-Dimethyl-*p*-benzoquinone (2,3-Me_2BQ) is a valuable chemical that is applied as a soft oxidizing and dehydrogenating agent and also as a synthon in preparing different complex products including pharmaceutical and biochemical substances. Keggin- and modified-type aqueous solutions of Mo-V-phosphoric heteropoly acids (Mo-V-P HPAs) with the gross compositions $H_{3+x}PMo_{12-x}V_xO_{40}$ (HPA-x) and $H_aP_zMo_yV_{x'}O_b$ (HPA-x'), respectively, possessing high oxidation potential and simplicity of regeneration can serve as effective soft oxidants for obtaining such *para*-quinone from 2,3-dimethylphenol (2,3-Me_2P). The synthesized HPA catalysts with different vanadium content were characterized by a number of analysis techniques, such as ^{31}P and ^{51}V NMR spectroscopy, potentiometry, titrimetry, and pH measurement. It was found that the predominant formation of 2,3-Me_2BQ instead of corresponding diphenoquinone (DPQ) at one-electron oxidation is achieved by a consecutive optimization of reaction conditions, the most important among them being organic solvent and molar ratio of vanadium(V) to substrate. As was shown, the substitution of HPA-x by HPA-x' allows one to increase the quinone selectivity and to decrease the optimal molar ratio of vanadium(V) to substrate. The highest yield of the desired quinone (97%) at total substrate conversion was obtained by using the biphasic water-benzene system at molar vanadium(V) to substrate ratio of 12. The temperature of 50 °C and an inert atmosphere were established to be the optimal reaction conditions. The aqueous HPA-10′ solution including the highest content of VO_2^+ ions proved to be the most efficient catalyst among investigated HPAs. Carrying out catalyst regeneration at a separate stage provides the preservation of its activity and selectivity at the initial level for at least ten cycles.

1. Introduction

Developing the processes of industrial multistage low-tonnage production of organic substances is an important area which intensifies nowadays all over the world [1,2]. Being potential products and 'platform molecules' in this area, quinones can serve as one- or two-electron acceptors and also participate in a wide range of biological redox processes, such as NAD- and FAD-dependent reactions, processes of photosynthetic and respiratory energy transduction, and in reactions catalyzed by a group of enzymes designated quinoproteins [3]. Due to the ability of quinones to transfer both electrons and protons, they also play an important biochemical role in understanding electron and proton movement.

2,3-Dimethyl-*p*-benzoquinone (2,3-Me_2BQ) is a valuable chemical which is applied as a sensitizer in photorefractive systems and amperometric sensors and as a soft oxidizing and dehydrogenating agent [4]. It is as well a very promising substrate for producing various medical and physiologically active substances. Owing to the presence of reactive C=C and C=O sites in the structure, 2,3-Me_2BQ may enter into diverse reactions including amination, acylation, alkylation and arylation as well as cycloaddition [5]. It allows one to apply this compound as useful synthon for synthesis of substances with antiparasitic [6,7], anticancer [8], and antioxidant [9–11] activities (Fig. 1). However, under conditions of redox processes, quinones and hydroquinones have no sufficient stability. As a result, the task of selective synthesis of benzoquinones has certain difficulties and requires of developing new methods for their preparation including environmentally safe catalytic technologies.

Selective oxidation of phenols is one of the most valuable reactions for preparing quinones with a simple structure, and a variety of different methods has emerged to date [4]. Previously, much attention has been paid on developing effective oxidizing systems on the basis of metal salts [12,13], transition metal complexes [14,15], oxide catalysts [16–18], microporous and mesoporous heterogeneous catalysts [19–24], with some of them showing excellent activity in oxidation of phenols. However, the insufficient stability and low activity at reusing

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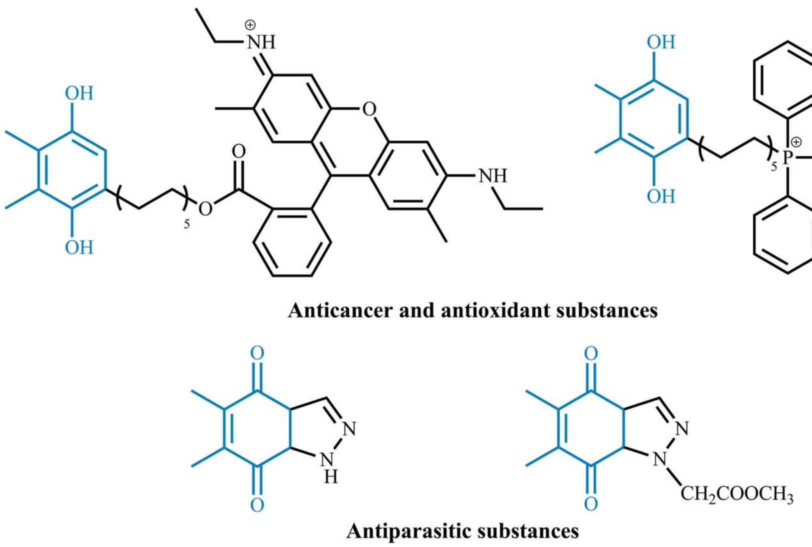

Fig. 1. Examples of valuable compounds obtained from 2,3-Me_2BQ.

along with hard regeneration conditions of these catalysts have limited their commercialization. The out-of-date processes based on oxidizing substituted anilines with MnO_2/H_2SO_4 at 10 °C or $Na_2Cr_2O_7/H_2SO_4$ at 20 °C are still used for preparing quinones [25]. As a consequence, further improvement of developed processes or investigation of alternative catalysts is required in this area.

Polyoxometalates (POM) are an extensive class of isopoly and heteropoly compounds, the properties of which can change broadly depending on elemental composition, the number of atoms in inorganic framework, relative position of atoms and their binding method, and also a counterion [26]. As a result, a large number of POMs currently exists, but only some of them are used in practice [27].

Today, the catalytic processes based on applying heteropoly (HP) compounds are an actively developing field of investigations [28–31]. Among HP-compounds used in oxidative and/or acid catalysis, the mixed-addenda Mo-V-phosphoric heteropoly acids (Mo-V-P HPAs, Fig. 2) attract significant attention as perspective oxidative [32–37] and bifunctional catalysts [38,39]. The interest of investigating such HP-compounds in catalysis has considerably increased lately due to the accumulation of data concerning their properties (especially owing to information dissemination on their reversible oxidability and simplicity of regeneration [40,41]). However, the solution both the general problems of this class of compounds (e.g. stability of catalysts) and the particular issues of their application for improvement of specific catalytic processes requires of extending investigations in this area.

In this work we investigated the synthesis of 2,3-Me_2BQ by oxidation of corresponding 2,3-dimethylphenol (2,3-Me_2P). The key to realize this reaction as the efficient catalytic one consists in applying catalysts possessing both a high oxidative ability and a possibility to rapid electron transfer. The shifting from acidic properties which are typical for all HPA groups to redox dominance due to the introduction into molybdenum-oxygen framework of vanadium(V) atoms (V^V) allows us to consider the aqueous Mo-V-P HPA solutions with Keggin $H_{3+x}PMo_{12-x}V_xO_{40}$ (HPA-x) and modified $H_aP_zMo_yV_{x'}O_b$ (HPA-x') gross compositions as promising homogeneous oxidative catalysts that can be used as soft oxidants for converting various organic compounds. Previously, we showed that this kind of catalysts exhibits excellent efficiency in some transformations including oxidation of trimethylphenol [42] and hydrolytic oxidation of cellulose [43]. At that, the choice of oxidant determines the efficiency and the practicality of systems, and molecular oxygen is regarded as a 'greenest oxidant'. This offers the significant opportunities for clean synthesis of fine and special chemicals [44].

This work is aimed at studying the effect of the composition of aqueous Mo-V-P HPA solutions and their oxidative properties as well reaction conditions on reaction time and product distribution during 2,3-Me_2BQ synthesis by oxidizing 2,3-Me_2P in order to obtain the maximal quinone selectivity and to ascertain the general patterns of this reaction. The major problem limiting the utility of homogeneous catalytic processes is the well-known difficulty in catalyst recovery and recycling. In our work we used a biphasic water-organic system that enables us to overcome the separation problem.

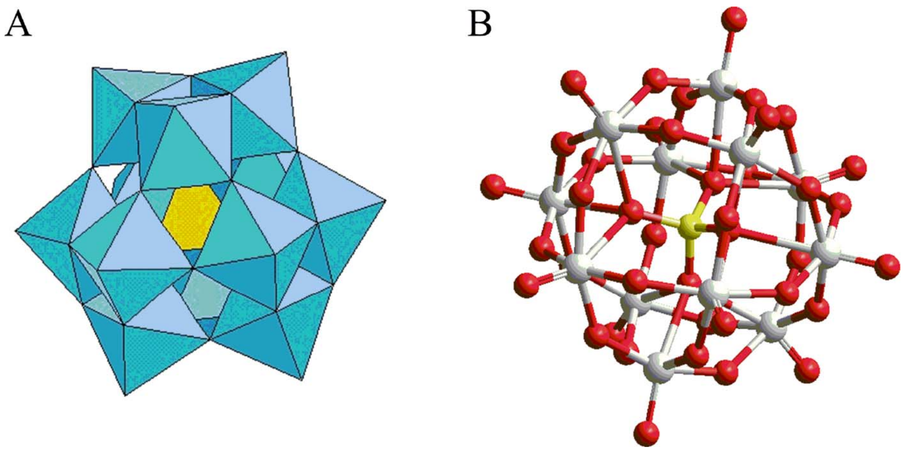

Fig. 2. Polyhedral (A) and component-bonding (B) models of α-Keggin polyoxoanion with general composition $[PM_{12}O_{40}]^{3-}$, M – structure-forming metal (Mo^{VI}, V^V).

2. Experimental

2.1. Chemicals

For synthesis of HPA solutions, 85 wt.% H_3PO_4 (99.4%), V_2O_5 (99%), MoO_3 (99%), and 30 wt.% H_2O_2 (special purity) all supplied by Sibreakhim (Novosibirsk) were used. 2,3-Me_2P (99%) was purchased from Aldrich. 2,3,5,6-Tetramethyl-*p*-benzoquinone (DQ) was from Merck-Schuchardt (99.9%) and was used as an internal standard in GC analysis. All organic solvents (~99%) were obtained from Sibreakhim and used as received.

2.2. Catalyst synthesis

The modified-type aqueous HPA-x' solutions of compositions $H_{13}P_3Mo_{15}V_6O_{74}$ (HPA-6′), $H_{10}P_3Mo_{18}V_7O_{84}$ (HPA-7′), $H_{11}P_3Mo_{18}V_8O_{87}$ (HPA-8′), and $H_{17}P_3Mo_{16}V_{10}O_{89}$ (HPA-10′) were prepared by the method of Odyakov et al. [45]. According to the method, vanadium(V) oxide, V_2O_5, was dissolved in cold distilled water, and a cold diluted H_2O_2 solution was added to the slurry at stirring. Upon gradual heating to room temperature, the resulting dark-red mixture of peroxo-vanadium compounds spontaneously decomposed with O_2 evolving, forming a dark-orange solution of decavanadic acid $H_6V_{10}O_{28}$. The obtained $H_6V_{10}O_{28}$ solution was stabilized by adding diluted H_3PO_4 solution with forming $H_9PV_{14}O_{42}$, as detailed in Eqs. (1) and (2).

In the next step, the prepared $H_9PV_{14}O_{42}$ solution was gradually introduced into boiling aqueous suspension of MoO_3 and H_3PO_4 under vigorous stirring (Eq. (3)). The resulting solution after the total $H_9PV_{14}O_{42}$ addition and complete MoO_3 dissolution was evaporated to required volume, giving homogeneous HPA-x' solution with a specified composition. The volume of prepared HPA solutions ranged within 0.25–0.32 L.

$$V_2O_5 \xrightarrow{+H_2O_2} VO(O_2)^+ + VO(O_2)_2^- \xrightarrow[-O_2]{} H_6V_{10}O_{28} \tag{1}$$

$$1.4H_6V_{10}O_{28} + H_3PO_4 \rightleftharpoons H_9PV_{14}O_{42} + 1.2H_2O \tag{2}$$

$$yMoO_3 + \left(z-\left(\frac{x'}{14}\right)\right)H_3PO_4 + \left(\frac{x'}{14}\right)H_9PV_{14}O_{42} + cH_2O \rightarrow H_aP_zMo_yV_{x'}O_b \tag{3}$$

To compare the catalytic activity, the low-vanadium Keggin-type aqueous solutions of $H_5PMo_{10}V_2O_{40}$ (HPA-2) and $H_7PMo_8V_4O_{40}$ (HPA-4) were also synthesized by a similar technique according to Eq. (4) in the volumes of 0.25 L [46].

$$(12-x)MoO_3 + 0.5xV_2O_5 + H_3PO_4 + 0.5xH_2O \rightarrow H_{3+x}PMo_{12-x}V_xO_{40} \tag{4}$$

2.3. Catalyst characterization

The composition of freshly prepared and spent solutions was investigated by ^{31}P and ^{51}V NMR spectroscopy on a Bruker AVANCE 400 high-resolution NMR spectrometer at 162.0 and 105.24 MHz, respectively, with 85% H_3PO_4 and $VOCl_3$ as external standards.

Redox potentials (E) and pH values of the aqueous HPA solutions were measured at room temperature using a pH-meter inoLab pH 730 (WTW, Germany). For pH registering, a combined pH-electrode 'SenTix 41' with an embedded temperature detector was used. The pH electrode was calibrated in the usual manner using buffers with a pH of 1.09 (Hamilton) and 4.01 (WTW). To measure the E values, a combined platinum electrode 'SenTix ORP' with a ceramic diaphragm was applied. The values of E are given in volts (V) relative to the Normal Hydrogen Electrode (NHE). Potential constancy of HPA solutions was attained in 3–4 min with an accuracy of ± 0.005 V; pH constancy was achieved in 4–5 min accurate within ± 0.01 pH units.

To obtain the reduced HPAs without pollution with extraneous compounds, prepared solutions in 35–40 mL volume were placed into temperature-controlled reactor and quantitatively reduced with a 10 M aqueous solution of hydrazine hydrate $N_2H_4{\cdot}H_2O$ at 70 °C until nitrogen evolution ceased. The necessary amount of hydrazine hydrate was calculated from Eq. (5) subject to total vanadium(V) content. The volume of nitrogen evolved was determined by a burette. In all experiments, the amount of nitrogen corresponded to the amount of N_2H_4 added with an accuracy of ± 1%.

$$4VO_2^+ + N_2H_4 + 4H^+ \rightarrow 4VO^{2+} + 4H_2O + N_2 \tag{5}$$

The concentration of vanadium(IV) (V^{IV}) in fresh and regenerated HPA solutions was determined by potentiometric titration with 0.1 N $KMnO_4$ in the presence of H_3PO_4 [47]. The average reduction degree of the solutions (m_{red}) was calculated according to Eq. (6), where '[HPA]' is the initial concentration of HPA solution.

$$m_{red} = \frac{[V^{IV}]}{x\times[HPA]} = \frac{[V^{IV}]}{[V^{IV}] + [V^{V}]} \tag{6}$$

To estimate the thermostability of solutions prepared (the temperature of solution decomposition, T_d), the sample of solution (50 mL) was heated in a thermostatic stainless steel autoclave to 130 °C under vigorous stirring. After keeping at this temperature for 1 h, the solution was cooled and filtered. In the absence of precipitation, heating was repeated with increasing temperature by 5 °C.

2.4. Catalyst testing

Oxidation of 2,3-Me_2P was carried out in a jacketed glass reactor under vigorous stirring (900 rpm) with a magnetic stir bar in a two-phase system composed of an aqueous HPA solution and an organic solvent with a dissolved substrate. In a typical experiment, the substrate (0.033 ÷ 0.15 g) was dissolved in an organic solvent (OS), and the resulting solution was introduced (entirely or dropwise) into reactor with a certain amount of HPA solution. The experiments were performed at different temperatures (25–50 °C) and molar ratio of vanadium(V) to substrate ($[n_{V^V}]/[Su]$) in the range of 4–21. The reactor was equipped with a reflux condenser to avoid the loss of water and organic solvent during the experiments. For studies under inert atmosphere, air was substituted by N_2 or CO_2, and a slow stream of inert gas was kept at the reactor inlet. In the course of reaction, a small volume of the reaction solution was periodically sampled, and then the conversion of 2,3-Me_2P and the yields (η) (or selectivities (S)) of products were determined by GC analysis. After the reaction was completed, the organic phase was separated from the catalyst solution in a separating funnel. The product traces were additionally removed from the aqueous phase by chloroform extraction (5 mL). Organic phase was washed twice with water to ensure the total catalyst separation. In some cases the content of catalyst components (Mo, V, P) in organic solution after catalyst removing was determined by ICP AES method using a Perkin Elmer Optima 4300 DV spectrometer. Their amount was within 10^{-8}–10^{-10} mol L^{-1}. The products were confirmed by comparison of their GC retention times, GC–MS patterns, and/or infrared spectra with those of the authentic samples.

2.5. Catalyst regeneration

After the experiments, the spent HPA solution was placed into a thermostatic stainless steel autoclave equipped with a glass beaker-insert. The Keggin-type HPA-4 solution was regenerated at the temperature of 140 °C and an oxygen pressure of 2–4 atm stirring for 35–40 min [48]. The reduced modified-type HPA-x' solutions and Keggin-type HPA-2 solution were oxidized at 170 °C for 20 min at the same oxygen pressure as for HPA-4. The regenerated HPA solutions were used for repeated synthesis of 2,3-Me_2BQ.

2.6. Analytical methods

Conversion of 2,3-Me_2P and product yields (selectivities) were determined by GC analysis using a Hromos GH-1000 chromatograph with a FID equipped with a St-WAX capillary column. DQ was used as an internal standard.

GC–MS spectra were recorded on an Agilent Technologies 7000 GC/MS Triple Quad instrument equipped with a GsBP1-MS capillary column. In addition, the isolated powdered products were also analyzed by infrared spectroscopy on a Vector 22 spectrometer using mixtures with KBr.

3. Results and discussion

3.1. Composition of HPA-x and HPA-x' solutions

Applying so-called 'peroxide' method to synthesize the described above Mo-V-P HPA solutions has provided the complete dissolution of the source oxides and the absence of extraneous substances (e.g., Na^+, Cl^-, SO_4^-) in comparison with other existing methods [49]. At that, according to the gross-composition of prepared HPA solutions, the increased amount of V^V and H_3PO_4 and also the atomic P/(Mo + V) ratio above 1/12 are the distinctive features of HPA-x' as compared to HPA-x.

^{31}P and ^{51}V NMR spectra of freshly prepared Keggin-type HPA-2 and HPA-4 solutions and also of modified-type HPA-7′ and HPA-10′ solutions are shown in Figs. 3 and 4, correspondingly.

As can be seen from the spectra in Figs. 3 and 4, both the HPA-x and HPA-x' solutions are the close in composition complex mixtures of individual heteropoly anions (HP-anions) containing different number of vanadium atoms.

The aqueous 0.40 M HPA-2 solution is an equilibrium mixture of individual Keggin-type anions $H_{x\text{-}1}PMo_{12\text{-}x}V_xO_{40}{}^{4-}$ with **x** of 1–3. The 0.20 M HPA-4 solution includes the indicated above Keggin-type anions with **x** of 1–5. In addition, the ^{51}V and ^{31}P NMR spectra of this solution contain broad lines at −544.8 and 0.53 ppm that can be attributed to the weakly bound $V^VO_2{}^+$ and $H_zPO_4{}^{(3-z)-}/H_3PO_4$ ions, respectively. These signals are weak, and their labeling becomes complicated due to overlapping the signals from individual Keggin-type anions. The broadening of these signals can be associated with exchange reactions progressing in solution between existing there different ions [50]. In the spectrum of the HPA-2 solution the line from $VO_2{}^+$ is very weak and practically invisible, but its intensity increases with increasing **x**.

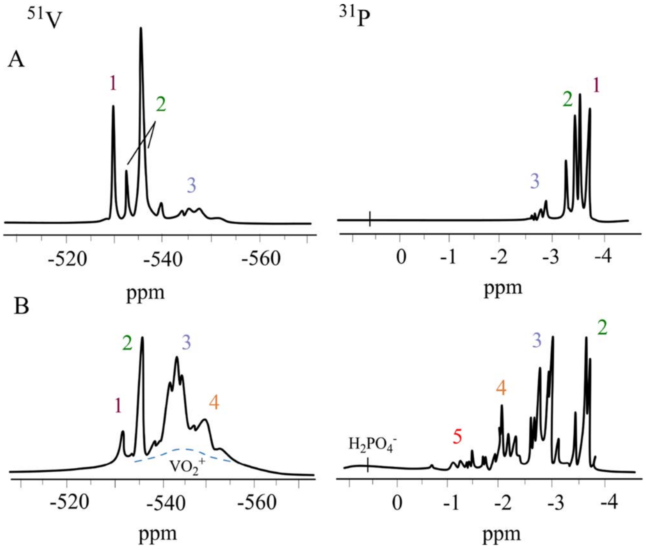

Fig. 3. ^{31}P and ^{51}V NMR spectra of aqueous Keggin-type HPA-x solutions: (A) 0.40 M HPA-2 and (B) 0.20 M HPA-4. The numbers 1–5 correspond to individual HP-anions with x of 1–5.

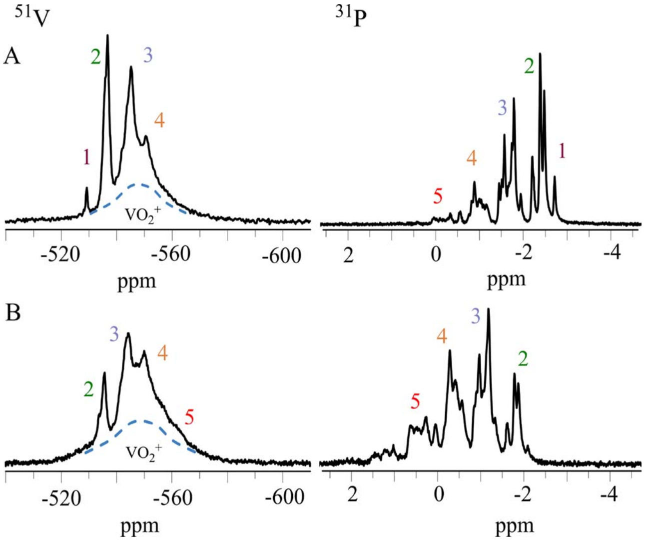

Fig. 4. ^{31}P and ^{51}V NMR spectra of aqueous modified-type HPA-x' solutions: (A) 0.25 M HPA-7′ and (B) 0.25 M HPA-10′. The numbers 1–5 correspond to individual HP-anions with x of 1–5.

According to the spectra in Fig. 4, the synthesized modified-type HPA-x' solutions have composition close to that of HPA-x ones. ^{31}P NMR spectrum of HPA-7′ solution consists of lines typical of Keggin-type HP-anions with **x** of 1–5 and gives an average solution composition close to $H_2PMo_9V_3O_{40}{}^{4-}$ [45]. Besides, there is a broad signal of $VO_2{}^+$ cation at 530–560 ppm overlapping with HPA lines in the ^{51}V NMR spectrum that complicates the precise determination of its concentration from such spectra. In the spectra of HPA-10′ solution there are the lines relating to the isomeric HP-anions with **x** of 2–5 as well a broad line from $VO_2{}^+$, with the abundance of high-vanadium HP-anions increasing. It allows concluding that HPA-x' solutions are actually a mixture of H_3PO_4 with different Keggin-type acids where the excess of vanadium(V) is present as $VO_2{}^+$ cations associated with HP-anions and $H_zPO_4{}^{(3-z)-}$. At that, for modified HPA solutions the ^{31}P NMR lines due to the individual HP-anions and the ^{51}V NMR lines from these anions shift downfield and upfield, respectively, relative to the same signals in aqueous Keggin-type solutions. These shifts are explained by the more protonation extent of existing in modified solutions HP-anions due to higher acidity of HPA-x'. In all spectra for every individual HP-anion except HPA-1 there is a 'fine structure' specified by the existence of positional isomers [51–53].

Thus, the prepared HPA-x and HPA-x' solutions contain the Keggin-type heteropoly anions $H_{x\text{-}1}PMo_{12\text{-}x}V_xO_{40}{}^{4-}$ with different number of vanadium atoms **x**, cations $VO_2{}^+$ and H^+, and also anions of phosphoric acid $H_zPO_4{}^{(3-z)-}$, with the latter getting distinctly visible only in the spectra of diluted solutions (with concentration of 0.05 mol L^{-1}) [45]. Moreover, the strong broadening in the presented NMR spectra of lines from $VO_2{}^+$ and $H_zPO_4{}^{(3-z)-}$ ions allows us to assume the possibility of exchanging between free and bonded states of these ions in HPA solutions, and also of forming different products of their association as outer-sphere complexes with HP-anions.

3.2. Physicochemical properties of HPA solutions

The ability of Mo-V-P HPA solutions to act as oxidants is based on reversible transformations of vanadium atoms: $V^V \leftrightarrow V^{IV}$ [54]. The possibility of partial reducing V^V to V^{IV} during V_2O_5 activation with H_2O_2 upon solution synthesis results in necessity to determine the exact V^V content. It was calculated as difference of total vanadium content (C_V) and concentration of V^{IV} ($C_{V^{IV}}$) with the latter being estimated by potentiometric titration. Amount of V^{IV} was also used to calculate the average reduction degree of solutions (m_{red}) after synthesis. The

Table 1
Physicochemical properties of freshly prepared HPA-x and HPA-x’ solutions.

HPA	C_{HPA}, M	C_V, M[a]	$C_{V^{IV}}$, M	C_{V^V}, M	*E*, V	pH	m_{red}·100%, %	T_d, °C[b]
$H_5PMo_{10}V_2O_{40}$	0.40	0.80	0.03	0.77	1.074	−0.19	3.8	190
$H_7PMo_8V_4O_{40}$	0.20	0.80	0.03	0.77	1.033	0.31	3.8	140
$H_{13}P_3Mo_{15}V_6O_{74}$	0.25	1.50	0.07	1.43	1.084	−0.32	4.7	185
$H_{10}P_3Mo_{18}V_7O_{84}$	0.25	1.75	0.09	1.66	1.097	−0.34	5.1	190
$H_{11}P_3Mo_{18}V_8O_{87}$	0.25	2.00	0.11	1.89	1.104	−0.32	5.5	185
$H_{17}P_3Mo_{16}V_{10}O_{89}$	0.25	2.50	0.12	2.38	1.112	−0.31	4.8	180

[a] Total vanadium content that is calculated as (**x** × C_{HPA}).
[b] Temperature of solution decomposition.

obtained data along with some other properties of prepared HPA solutions are presented in Table 1.

According to Table 1, a somewhat lower vanadium(V) content compared with calculated value is observed in prepared solutions. It is an evidence for partial reduction of V^V with H_2O_2 to V^{IV}, with the V^{IV} content being less than 6% of the total one. All solutions both Keggin and modified-type compositions are strong Brønsted acids with pH values below 1. At that, the acidity of HPA-x’ solutions is higher as compared to HPA-x that is explained by more content of H_3PO_4. The excess of H_3PO_4 seems to exist in modified solutions as partially dissociated anions $H_zPO_4^{(3-z)-}$ connected with HP-anions and VO_2^+ ions. It results in stabilizing additional VO_2^+ ions and growing their steadiness to $V_2O_5{\cdot}nH_2O$ deposition. As a consequence, such solutions acquire a higher thermostability (see T_d parameter in Table 1) that is of primary importance to achieve minimal m_{red} values after their regeneration [55].

The solutions synthesized also possess oxidation potential values higher than 1 V. It is an important feature that allows using these HPA solutions as oxidants. Fig. 5 demonstrates the dependence of *E* from vanadium(IV) content for 0.25 M HPA-7′ and 0.20 M HPA-4 solutions. It is evident from the figure that high vanadium content in HPA-x’ solutions provides a less sharply decrease of *E* values upon their reduction. It allows us to consider HPA-x’ as promising oxidants for catalytic reactions. To obtain the depicted in Fig. 5 curves, the HPA-7′ and HPA-4 solutions were partially reduced with N_2H_4, measuring the $[V^{IV}]$ content and oxidation potential after each reduction.

3.3. *Effect of reaction conditions on the reaction time and product distribution*

The synthesized Mo-V-P HPA-x and HPA-x’ solutions have been tested as catalysts for oxidation of 2,3-Me_2P to corresponding 2,3-Me_2BQ. The influence of various reaction parameters, in particular, organic solvent, temperature, atmosphere (inert or oxygen-containing one), and molar $[n_{V^V}]/[2,3\text{-}Me_2P]$ ratio was examined in details.

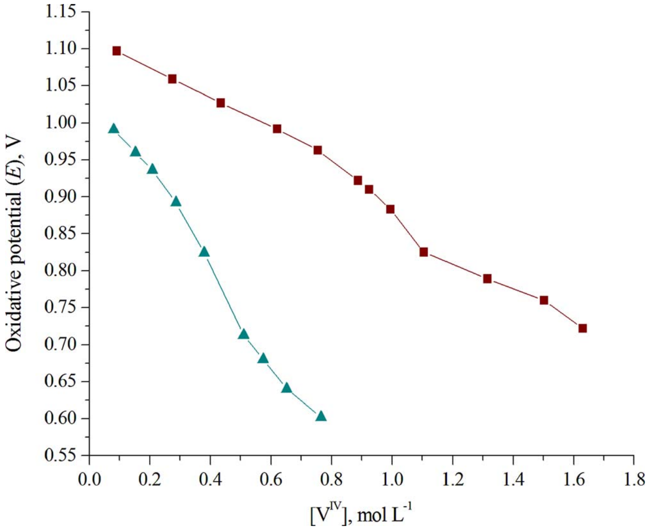

Fig. 5. Oxidative potential (*E*) dependence on vanadium(IV) concentration for 0.25 M HPA-7′ (■) and 0.20 M HPA-4 (▲) solutions.

Table 2
Effect of solvents on product distribution upon 2,3-Me_2P oxidation to 2,3-Me_2BQ.[a]

#	Solvent	Product selectivity, %		
		2,3-Me_2BQ	DPQ	PPO
1[b]	without OS	8	89.4	2.6
2[c]	Heptane	9.6	77.2	13.2
3[d]	Cyclohexane	13.1	74.9	12.0
4	Benzene	40.4	45.6	14.0
5	Toluene	37.3	48.4	14.3
6	Trichloromethane	28.4	56.6	15.1
7	Trichloroethene	36.8	45.4	17.8
8	1-Pentanol	12.8	64.0	23.2
9	1-Hexanol	17.3	63.1	19.6
10	1-Octanol	20.4	61.4	18.2
11	2-Octanone	21.2	59.7	19.1
12	3-Hexanone	18.6	62.8	18.6
13	1-Etoxyoctane	15.4	66.7	17.9
14	1-Ethoxypentane	18.2	61.3	20.5
15	Ethyl acetate	21.1	57.3	21.6
16	Ethyl Benzoate	24.3	57.1	18.6
17	Hexanoic acid	28.2	51.6	20.2
18	Heptanoic acid	27.6	50.9	21.5
19	Octanoic acid	24.5	56.7	18.8

[a] Reaction conditions: 0.25 M $H_{13}P_3Mo_{15}V_6O_{74}$ (HPA-6′) 7.5 mL (n_{V^V} = 1.07·10^{-2} mol), 2,3-Me_2P 0.066 g, air atmosphere, temperature 25 °C, organic solvent volume 5.6 mL, molar $[n_{V^V}]/[2,3\text{-}Me_2P]$ ratio 20, reaction time 65 min. Substrate conversion is 100%.
[b] Substrate conversion is 18%.
[c] Substrate conversion is 93%.
[d] Substrate conversion is 98%.

Our initial experiments were focused on optimizing organic solvent (OS). The investigation of this parameter was performed in the presence of 0.25 M HPA-6′ solution ($H_{13}P_3Mo_{15}V_6O_{74}$) at room temperature. The results of solvent screening are summarized in Table 2.

The results presented in Table 2 indicate that organic solvent is an active reaction member which significantly affects the selectivity of the desired product. When using a solvent-free system, the reaction hardly proceeded and led to quinone formation with yield of less than 2%. Among the solvents examined, benzene and toluene gave the maximal 2,3-Me_2BQ selectivity that was higher than 37%. The representatives of carboxylic acids, esters and ketones showed moderate selectivities. In contrast, nonpolar alkanes, such as heptane and cyclohexane, were not suitable for the reaction. It is likely to be explained by their weak coordination to the substrate molecules and the reaction intermediates. Under the indicated in Table 2 reaction conditions, the preferred formation of 2,2′,3,3′-tetramethyl-4,4′-diphenoquinone (DPQ) was observed in all cases. Low-molecular aromatic polyethers with linear structure (phenol ether resins, PPO) were also registered as by-products (Fig. 6).

As shown in Table 2, the desired quinone was significantly obtained when the reaction was performed using aromatic hydrocarbons and

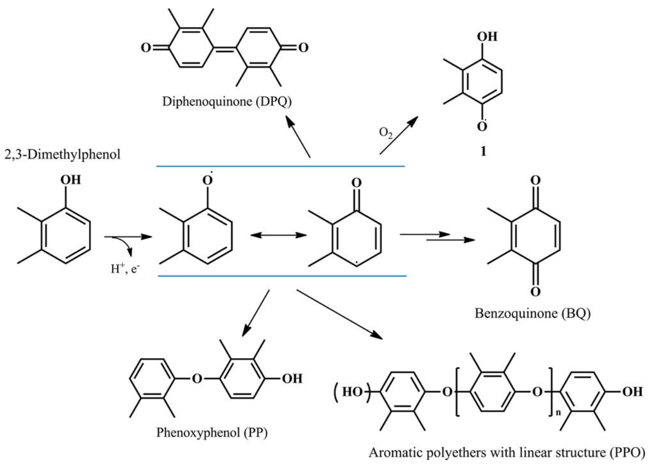

Fig. 6. Products obtained upon 2,3-Me_2P oxidation.

halogen-containing alkenes. It can be assumed that the selection of optimal OS allows one to assure the effective solvation of substrate molecules and intermediate compounds via donor-acceptor interactions, destroying phenol self-associates and complicating radical recombination. At that, the initial 2,3-Me_2P is an electron donor, whereas benzene, toluene, and halogen-containing alkenes are electron acceptors. Another important property providing the efficient interaction of substrate and the optimal OS is their high degree of polarizability. On the basis of obtained 2,3-Me_2BQ selectivity and higher acceptor properties compared to toluene, benzene was used by us for further experiments as a model solvent. The selection of organic solvents was based on their low water solubility, boiling temperature above 70 °C, and stability into acid oxidizing media.

At the next stage we investigated the influence of reaction temperature. Raising the temperature from 25 to 50 °C enabled increasing the selectivity of desired product from 40 to ~70% and decreasing the PPO formation (Fig. 7). It also favored the reduction in reaction time by about 1.5 times (from 60 to 36 min). We believe that the observed rise of 2,3-Me_2BQ selectivity and the acceleration of the reaction can be attributed to increasing $VO_2{}^+$ ions content due to their formation via Eq. (7) and also raising mobility of these ions. According to the data [56,57], the degree of such dissociation in HPA-1 solution is slight, but its raising is observed with increasing **x** value and solution acidity and decreasing solution concentration. It allows us to suppose that it is $VO_2{}^+$ ions that take part in oxidation in the first place. The experiments were carried out in the presence of HPA-6′ solution possessing high content of $VO_2{}^+$ ions.

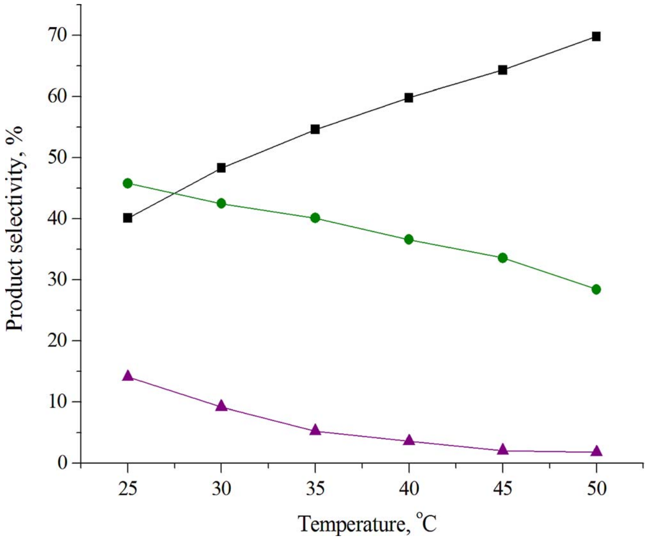

Fig. 7. Product selectivity dependence on reaction temperature in the presence of 0.25 $H_{13}P_3Mo_{15}V_6O_{74}$ (HPA-6′) solution: (■) – 2,3-Me_2BQ, (●) – DPQ, (▲) – PPO. Reaction conditions: catalyst 7.5 mL (n_{V^V} = $1.07{\cdot}10^{-2}$ mol), 2,3-Me_2P 0.066 g, air atmosphere, benzene 5.5 mL, molar $[n_{V^V}]/[2,3\text{-}Me_2P]$ ratio 20. Substrate conversion is 100%.

Table 3
Effect of reaction atmosphere on product distribution upon 2,3-Me_2P oxidation to 2,3-Me_2BQ.[a]

Atmosphere	Product selectivity, %	
	2,3-Me_2BQ	DPQ
N_2	58.8	37.3
Air	54.3	39.3
CO_2	58.7	38.2

[a] Reaction conditions: 0.20 M $H_7PMo_8V_4O_{40}$ (HPA-4) 7 mL (n_{V^V} = $5.39{\cdot}10^{-3}$ mol), 2,3-Me_2P 0.033 g, 50 °C, benzene 5 mL, molar $[n_{V^V}]/[2,3\text{-}Me_2P]$ ratio 20, reaction time 40 min. Substrate conversion is 100%.

$$(13-x)H_{3+x}PMo_{12-x}V^{V}_{x}O_{40} + 12H^{+} \leftrightarrow (12-x)H_{2+x}PMo_{13-x}V^{V}_{x-1}O_{40} + 12V^{V}O_2^{+} + H_3PO_4 + 12H_2O \tag{7}$$

$$\begin{array}{ccccc} V^{IV}O^{2+} & + \; H_2\,O \leftrightarrow & V^{V}O_2^{+} & + \; 2H^{+} + \bar{e} & \\ \upharpoonleft\!\downharpoonright & & \upharpoonleft\!\downharpoonright & & \\ H_{x+m+3}PMo_{12-x}V^{IV}_{m}V^{V}_{x-m}O_{40} & \leftrightarrow & H_{x+m+2}PMo_{12-x}V^{IV}_{m-1}V^{V}_{x-m+1}O_{40} & + \; H^{+} + \bar{e} & \end{array} \tag{8}$$

Continuing our experiments on optimizing reaction conditions in the presence of 0.20 M Keggin-type HPA-4 solution, we also ascertained that application of inert atmosphere has no positive influence on the reaction time, but it increases the 2,3-Me_2BQ selectivity (Table 3). The oxidation of 2,3-Me_2P to 2,3-Me_2BQ can be performed in air atmosphere. However, oxygen absence results in raising the quinone selectivity by 4% and also decreases the PPO formation. The observed effect of inert atmosphere can be explained by the suppression of forming unstable peroxide compounds arising from the interaction of intermediate radicals with O_2. The decomposition of such compounds leads to receiving additional oxygen-containing intermediates that can take part in PPO formation (see Fig. 6, **1**). Based on product structures, here we suppose that the 2,3-Me_2P oxidation follows radical mechanism with forming several intermediate radicals.

Since the vanadium(V) atoms act as oxidation sites in HPA solutions, the predominant formation of 2,3-Me_2BQ can be achieved by using optimal oxidant (V^V) to substrate molar ratio. The molar $[n_{V^V}]/[2,3\text{-}Me_2P]$ ratio was examined in a wide range (from 4 to 21) in the presence of 0.20 M HPA-4 solution because V^V can be a part of both $V^VO_2{}^+$ ions and HP-anions (Table 4, Fig. 8).

As can be seen from Table 4, the change in indicated ratio affects significantly both the reaction time and the product distribution. Increasing V^V content promotes more rapid substrate conversion and favors higher 2,3-Me_2BQ selectivity. When using low vanadium(V) to substrate molar ratio, the reaction hardly proceeded and gave incomplete substrate conversion. It allows us to conclude that if catalysts do not possess the enough amounts of $V^VO_2{}^+$ ions, the intermediate radicals mainly recombine thus resulting in predominant formation of by-products. This testifies that the oxidation of 2,3-Me_2P in the presence of HPA solutions passes through stepwise radical mechanism, with the increase of vanadium content promoting the decrease of radical recombination [58]. At that, the rapid reduction of presented in solution $V^VO_2{}^+$ ions to $V^{IV}O^{2+}$ is expected to result in changing limiting stage of reaction. The initial rapid process of electron transfer from substrate to oxidant ($V^VO_2{}^+$) is substituted by slow exchange processes according to Eq. (8). As a result, incomplete substrate conversion and predominant DPQ formation are observed in such cases (at molar $[n_{V^V}]/$

Table 4
Effect of molar $[n_{V^V}]/[Su]$ ratio on product distribution upon 2,3-Me_2P oxidation to 2,3-Me_2BQ.[a]

#	V_{kat}, mL	n_{V^V}, mol	$[n_{V^V}]/[Su]$	Conversion, %	*t*, min	Product selectivity, %[b]		
						2,3-Me_2BQ	DPQ	PP[c]
1	4.2	0.00321	4	13.4	75	8.7	63.2	5.1
2	8.3	0.00642	8	28.4	75	16.8	59.3	5.2
3	10.4	0.00802	10	39.1	70	24.3	54.0	4.8
4	12.5	0.00963	12	54.3	70	31.6	52.7	2.1
5	14.6	0.01123	14	83.2	55	38.3	51.3	0.7
6	15.6	0.01203	15	91.6	50	45.3	46.9	0.4
7	16.7	0.01284	16	97.3	50	53.2	40.8	–
8	17.7	0.01364	17	100	45	56.2	38.6	–
9	18.8	0.01444	18	100	42	57.5	38.2	–
10	19.8	0.01524	19	100	42	58.1	37.7	–
11	20.8	0.01604	20	100	40	58.9	37.1	–
12	21.9	0.01685	21	100	38	59.6	36.6	–

[a] Reaction conditions: 0.20 M $H_7PMo_8V_4O_{40}$ (HPA-4) solution (c_{V^V} = 0.77 mol L^{-1}), 2,3-Me_2P 0.099 g, atm. N_2, 50 °C, benzene, organic solvent volume 0.75·V_{kat}.
[b] The remaining content of products corresponds PPO.
[c] 2,3-dimethyl-4-(2′,3′-dimethylphenoxy)phenol.

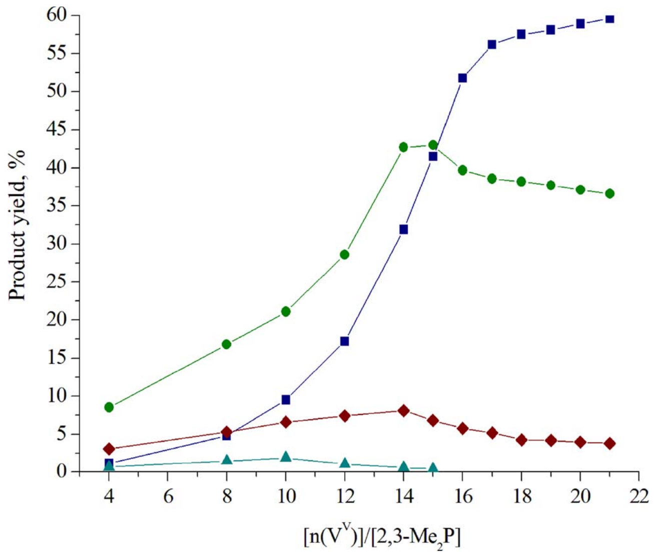

Fig. 8. Product distribution dependence on molar $[n_{V^V}]/[Su]$ ratio in the presence of 0.20 M $H_7PMo_8V_4O_{40}$ (HPA-4) solution. Reaction conditions: catalyst (c_{V^V} = 0.77 mol L^{-1}), 2,3-Me_2P 0.099 g, atm. N_2, temperature 50 °C, benzene, organic solvent volume 0.75·V_{kat}. Products: ● – DPQ, ■ – 2,3-Me_2BQ, ♦ – PPO, ▲ – PP.

[2,3-Me_2P] ratio ≤ 15, Fig. 8). It can be expected that application of high-vanadium HPA-x’ solutions will allow one to decrease the optimal vanadium(V) to 2,3-Me_2P molar ratio since such solutions contain more VO_2^+ amount. Note that at using molar ratio lesser 16 the small amounts of 2,3-dimethyl-4-(2′,3′-dimethylphenoxy)phenol (PP) were detected after experiments (Fig. 6).

3.4. Effect of HPA composition on the reaction time and product distribution

As can be seen from Section 3.1, the HPA solutions are complex equilibrium mixtures of different particles. Taking into account the decisive influence of catalyst composition on selectivity of desired quinone and reaction time, we investigated the 2,3-Me_2P oxidation in the presence of six synthesized HPA solutions with different vanadium content under the obtained optimal conditions. As was noted above, the vanadium(V) atoms in HPA solutions can exist as VO_2^+ ions and also be a part of HP-anions, which affects the observable 2,3-Me_2BQ selectivity. So, the effect of HPA solution composition on the reaction was determined in experiments where the HPA volume was calculated in such a manner that it provided an equal content of V^V atoms in the solutions. The obtained results of 2,3-Me_2BQ selectivity depending on the used HPA solution are shown in Table 5.

According to Table 5, under identical reaction conditions the reaction time and 2,3-Me_2BQ selectivity change considerably by using different HPA solutions, in spite of the equal V^V content in solutions and the close values of their oxidation potentials. Both the selectivity of 2,3-Me_2BQ formation and the reaction rate rise with an increase in the number of vanadium atoms **x** in HPA gross-composition: HPA-2 > HPA-4 > HPA-6′ > HPA-7′ > HPA-8′ > HPA-10′. When using the Keggin-type HPA solutions the reaction slowly proceeded and gave 2,3-Me_2BQ with selectivity only about 50%. It can be explained by the fact that the V^V atoms are present in such solutions mainly as a part of HP-anions (see Fig. 3). On the other hand, when oxidation of 2,3-Me_2P was performed in the presence of HPA-x’ solutions possessing high content of VO_2^+ ions stabilized by H_3PO_4, the predominant formation of desired quinone was observed.

The results obtained let us suppose that during the reaction the initial electron transfer from the substrate molecules occurs rapidly

Table 5
Effect of HPA composition on 2,3-Me_2BQ selectivity and reaction time.[a]

HPA	C_{HPA}, M	C_{V^V}, M	V_{kat}, mL	E_0, V	E_{fin}, V[b]	$S_{2,3\text{-}Me_2BQ}$, %	*t*, min
$H_5PMo_{10}V_2O_{40}$	0.40	0.77	17.7	1.074	0.738	43.5[c]	50
$H_7PMo_8V_4O_{40}$	0.20	0.77	17.7	1.033	0.786	56.4	45
$H_{13}P_3Mo_{15}V_6O_{74}$	0.25	1.43	9.5	1.084	0.958	72.2	36
$H_{10}P_3Mo_{18}V_7O_{84}$	0.25	1.66	8.2	1.097	0.973	78.4	35
$H_{11}P_3Mo_{18}V_8O_{87}$	0.25	1.89	7.2	1.104	0.986	83.1	32
$H_{17}P_3Mo_{16}V_{10}O_{89}$	0.25	2.38	5.7	1.112	0.993	92.1	32

[a] Reaction conditions: HPA solution, n_{V^V} = 0.0136 mol, 2,3-Me_2P 0.099 g, atm. N_2, 50 °C, benzene, organic solvent volume 0.75·V_{kat}. Substrate conversion is 100%.
[b] Oxidation potential after reaction.
[c] Substrate conversion is 92.3%.

Table 6
Many-cycle testing of catalytic system HPA-10′/benzene upon 2,3-Me_2P oxidation to 2,3-Me_2BQ.[a]

#[b]	$[n_{V^V}]/[Su]$	V_{kat}, mL	E_0, V	pH_0	E_{fin}, V	Method of Su addition	$S_{2,3}$-Me_2BQ, %	t, min
1	14	7.9	1.051	−0.24	0.952	once	91.8	32
2	13	7.3	1.052	−0.26	0.946	once	91.5	32
3	12	6.7	1.047	−0.23	0.942	once	90.9	34
4	13	7.3	1.049	−0.25	0.934	dropwise[c]	97.8	30
5	12	6.7	1.047	−0.23	0.926	dropwise	97.6	30
6	11	6.2	1.051	−0.26	0.920	dropwise	96.6	30
7	12	6.7	0.985[d]	−0.15	0.858	dropwise	94.1	30
8	12	6.7	0.933[e]	−0.01	0.806	dropwise	87.4	32
9	12	6.7	1.048	−0.24	0.924	dropwise	97.3	30
10	12	6.7	1.051	−0.26	0.921	dropwise	97.4	30

[a] Reaction conditions: 0.25 M $H_{17}P_3Mo_{16}V_{10}O_{89}$ (HPA-10′) solution, $c_{V^V} = 2.16\ mol\ L^{-1}$, 2,3-$Me_2P$ 0.15 g, atm. N_2, 50 °C, benzene, organic solvent volume $0.75 \cdot V_{kat}$. Substrate conversion is 100%.

[b] Each cycle contains the oxidation of the substrate, the separation of the catalyst from the reaction products and the regeneration of the catalyst by oxygen.

[c] The dropwise substrate addition was performed during 25 min.

[d] The catalyst was reduced with a 10 M N_2H_4 solution to $m_{red} = 0.308$.

[e] The catalyst was reduced with a 10 M N_2H_4 solution to $m_{red} = 0.362$.

mainly onto the readily accessible weakly-bound VO_2^+ ions. As their concentration decreases, the complex stages of electron exchange between the VO^{2+} ions formed during the reaction and V^V atoms present in HPA-ions get limiting. At that, the reaction rate decreases, and the rate of interaction between the reaction intermediates begins to exceed the rate of VO_2^+ forming. The best selectivity of 2,3-Me_2BQ in 92% at total substrate conversion was obtained in the presence of HPA-10′. In this case the formation of PPO was not observed. Note that the final E values of HPA-x' solutions after reaction are higher than those of HPA-x. The high E_{fin} values indicate the possibility of decreasing the optimal $[n_{V^V}]/Su$ molar ration below 17 for such solutions.

3.5. Many-cycle catalyst testing

In the final series of experiments, the optimal HPA-10′/benzene catalytic system was investigated in detail in terms of catalyst stability and reusability. Some reaction parameters, such as oxidation potential E, vanadium(V) to substrate molar ratio, and the method of substrate introducing, were varied during many-cycle testing of the catalyst (Table 6).

It is well known that the redox potential of HPA solutions E decreases upon the substrate oxidation and increases during the catalyst regeneration. In contrast, the pH value in the course of the same reactions goes through the inverse alterations. As can be seen from Table 6, the regenerated HPA-10′ solution has the decreased E_0 and increased pH values as compared to freshly prepared one (see Section 3.2, Table 1). It is explained by the fact that after the regeneration the attained value of V^{IV} concentration in catalyst solution (the average reduction degree of solution m_{red}) is higher compared to that obtained after synthesis. In regenerated solution the m_{red} value increases from 0.048 to 0.135 (from 4.8 to 13.5%) and remains at this level in the next cycles. The observed rise in m_{red} has no influence on the selectivity of desired product since it is compensated by sufficient vanadium(V) to substrate molar ratio.

The results presented in Table 6 show that applying HPA-10′ solution having the highest content of VO_2^+ ions among the synthesized ones makes it possible to reduce the optimal molar ratio to 12 (or up to 1.5, if to consider it as [HPA]/[Su]). The dropwise substrate addition provides the increase of 2,3-Me_2BQ selectivity at least 6% compared to the addition at once. The observed rise of product selectivity can be explained by a significant decrease in instantaneous concentration of substrate at such method of addition. The reduction of the catalyst solution before reaction to $m_{red} \sim 0.3$ (30%) results in moderate decrease of 2,3-Me_2BQ selectivity whereas the further reduction decreases the catalyst activity considerably.

The ^{31}P NMR spectrum of the regenerated HPA-10′ solution contains groups of lines of the same Keggin-type anions as the freshly prepared one. This spectrum is shifted by 2.3–3.0 ppm downfield after reduction of the solution to $m_{red} \sim 0.135$ due to an increase of paramagnetic ion VO^{2+} concentration and protonation of HP-anions. Under the optimized reaction conditions, the highest 2,3-Me_2BQ selectivity is 97%. The catalyst retains stability and selectivity at least 10 cycles. Note that in absence of HP-anions the regeneration of VO_2^+/VO^{2+} oxidation system does not occur.

4. Conclusions

The efficient method of 2,3-Me_2BQ synthesis via two-stage oxidation of 2,3-Me_2P in the presence of homogeneous Mo-V-P heteropoly acid catalysts has been demonstrated. The consecutive optimization of reaction parameters was shown to provide the transition from forming diphenoquinone that is observed as the primary product to dominating 2,3-Me_2BQ. It was found that applying appropriate organic solvent (aromatic hydrocarbons, halogen-containing alkenes) allows one to increase considerably the selectivity of the desired product likely due to the effective solvation of the substrate and the intermediate compounds via donor-acceptor interactions. Among the solvents examined, in this paper we used benzene as a model solvent as it showed both high selectivity and acceptor properties. The inert atmosphere was found to exert no effect on the reaction time, however, it affects favorably the selectivity of desired quinone.

The results obtained suggest that V^V atoms are an indispensable component for the phenol oxidation. As shown by the search for optimal HPA composition with the use of Keggin-type $H_5PMo_{10}V_2O_{40}$ and $H_7PMo_8V_4O_{40}$, and also modified-type high-vanadium $H_{13}P_3Mo_{15}V_6O_{74}$, $H_{10}P_3Mo_{18}V_7O_{84}$, $H_{11}P_3Mo_{18}V_8O_{87}$, and $H_{17}P_3Mo_{16}V_{10}O_{89}$, the highest values of reaction rate and 2,3-Me_2BQ selectivity are observed in the presence of HPA-10′ solution possessing the largest content of VO_2^+ ions. The substitution of HPA-4 solution by HPA-10′ one allows decreasing the optimal $[n_{V^V}]/Su$ molar ratio from 17 to 12. At the temperature of 50 °C under optimized conditions, 2,3-Me_2BQ was produced with 97% selectivity at 100% 2,3-Me_2P conversion. Virtually no polymerization of the substrate occurs at that. The reduced HPA-10′ catalyst can be easily separated, effectively regenerated by O_2 and reused at least 10 cycles. The acid function of HPA catalysts is also important for the total catalytic process. It provides catalyst stability and allows us to perform rapid HPA-10′ regeneration at temperatures up to 170 °C. It should be noted that in our further investigation we will expand the experiments on solvent optimization towards composition, structure, ecological compatibility, and physicochemical properties of different solvents and find the most appropriate solvent taking into account the obtained data.

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