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Trimethyl-1,4-Benzoquinone Synthesis via 2,3,6-Trimethylphenol Catalytic Oxidation by Oxygen in the Presence of Non-Keggin-Type Mo-V-Phosphoric Heteropoly Acid Solutions

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Abstract: In the present study, the modified (non-Keggin-type) aqueous solutions of Mo-V-phosphoric heteropoly acids $H_aP_zMo_yV_{x'}O_b$ (HPA-*x'*) were applied as homogeneous catalysts for the two-stage oxidation of TMP (2,3,6-trimethylphenol) by oxygen into TMQ (2,3,5-trimethyl-1,4-benzoquinone), the latter being the key intermediate in the synthesis of vitamin E. The TMQ yield was analyzed regarding solvent type, reaction temperature, molar HPA-*x'*:TMP ratio, and the concentration of vanadium (V) in the HPA-*x'* solution. The TMQ yield was found to depend strongly on the catalyst redox potential and the rate of electron transfer. The results obtained enabled to establish the optimal reaction conditions as well as to suggest the reaction mechanism. In the target reaction, which proceeds in the two-phase system, the TMQ yield is higher than 99%. After phase separation, the catalyst is rapidly regenerated by oxygen and reused.

Key words: Trimethyl-1,4-benzoquinone, catalytic oxidation, heteropoly acid, homogeneous catalysis.

1. Introduction

At present novel catalytic technologies are often applied to improve the existing industrial processes as well as to develop new energy saving and low-wasted technologies [1, 2]. They are of great importance for the industry of fine chemicals and pharmaceuticals, producing organics of a rather complex structure such as pesticides, dyes, aromas, vitamins and medicines [3]. Most often complex organic products are synthesized via technologies, which have many stages and produce harmful effluents and wastes. All these technologies are characterized by the high values of E-factor, which is the ratio of wastes and unreacted substrates to the useful product, and thus reflects the environmental safety of technology in whole [4]. Vitamin E synthesis is an example of such many-stage technology, whereas worldwide annual production of vitamin E exceeds 25,000 tons [5].

At present in industry, vitamin E is synthesized from TMQ (2,3,5-trimethyl-1,4-benzoquinone) [5]. During several decades, the TMQ is produced via homogeneous catalytic oxidation of TMP (2,3,6-trimethylphenol) by oxygen or oxygen-containing gas in the two-phase system, an aqueous solution of $CuCl_2$ (with additions of Li^+, NH_4^+ chlorides and other salts) being used as catalyst [6]. This catalyst has several disadvantages:

(1) The catalyst partially chlorinates a desired product TMQ into harmful to one's health chlorinated quinones, which are to be separated and neutralized to avoid their presence in the final product—vitamin E. It

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is very important, because the chlorinated quinones may react with proteins and DNA thus damaging them.

(2) A rather low activity of Cu^{II}-chloride catalysts (and thus low productivity) requires large reactor volumes and considerable energy consumption per product unit.

The above mentioned disadvantages make the industrial TMQ synthesis environmentally unsafe and increase the production cost of vitamin E. In this connection, the development of an alternative environmentally benign process for the production of TMQ is a real challenge.

In the last 20 years significant research effort has been focused on the development of new catalysts for the TMQ synthesis. A number of homogeneous and heterogeneous oxidative catalysts were suggested instead of copper chloride, such as Keggin-type heteropoly acids ($H_{3+x}PMo_{12-x}V_xO_{40}$) [7], phthalocyanines [8-10], molecular sieves K-OMS-2 [11], Fenton’s reagent [12], mesoporous titanosilicate heterogeneous catalysts [13-18], etc.. Most of them provide a rather high selectivity of TMP oxidation and solve the chlorination problem. However, all above mentioned catalysts have other disadvantages. Some of catalysts show comparatively low productivity and duration of target reaction and/or catalyst regeneration. Other catalysts undergo the rapid deactivation, or their active component is washed out into the reaction solution. Therefore, at present in industry the TMP is still oxidized to TMQ in the presence of copper (II) chloride.

HPA (heteropoly acids) are considered to be promising catalysts for this reaction due to their well known successful performance in catalysis [19]. There are many studies related to the HPA application in, e.g., propylene [20] and phenyl acetylene [21] hydration, tetrahydrofuran polymerization [22], 9,10-anthraquinone synthesis [23], as well as in other reactions of fine chemistry [24] yielding medical preparations [21] and vitamins [25].

At present, the modified (non-Keggin-type) solutions of Mo-V-P HPA (HPA-x') with formula $H_aP_zMo_yV_{x'}O_b$ (where $z > 1$; $x' > 4$), possessing a redox potential E_0 higher than 1.0 V, attract a lot of research attention as reversible oxidants. These solutions demonstrate a rather good thermal stability up to 170 °C, and there is no the vanadium-containing deposits during catalyst regeneration at this temperature in comparison with Keggin-type heteropoly acids ($H_{3+x}PMo_{12-x}V_xO_{40}$ = HPA-x ($x = 2 \div 6$), Fig. 1) [26, 27]. Also HPA-x' solutions have a higher vanadium content (above 2 M). It results in increasing the amount of oxidized substrate and enhancing catalyst productivity [28]. Owing to their high stability, the HPA-x' solutions can go through many times repeated redox conversions, and therefore may be used in many cycles for quite a long time.

After regeneration the modified HPA-x' solutions completely recover their initial properties [29]. With this regard the non-Keggin-type HPA-x' solutions seem to be promising catalysts for the organic substrates oxidation by oxygen.

The oxidation of various substrates (Su) involving HPA-x' solutions consist of two stages (Eqs. (1) and (2)) that are considered as a catalytic cycle (Eq. (3)):

$$^{m}/_{2}\,\mathrm{Su} + {}^{m}/_{2}\,\mathrm{H_2O} + \mathrm{HPA}\text{-}x' \longrightarrow {}^{m}/_{2}\,\mathrm{SuO} + \mathrm{H}_m\mathrm{HPA}\text{-}x' \quad (1)$$

$$\mathrm{H}_m\mathrm{HPA}\text{-}x' + {}^{m}/_{4}\,\mathrm{O_2} \longrightarrow \mathrm{HPA}\text{-}x' + {}^{m}/_{2}\,\mathrm{H_2O} \quad (2)$$

$$\mathrm{Su} + \tfrac{1}{2}\,\mathrm{O_2} \xrightarrow{\mathrm{HPA}\text{-}x'} \mathrm{SuO} \quad (3)$$

In stage (1), a substrate (Su) is oxidized by HPA-x' solution yielding the desired product (SuO) that is separated from the reduced form of HPA-x' (H_mHPA-x'). The latter is oxidized with O_2 in stage (2) at elevated temperature and under pressure [30] closing

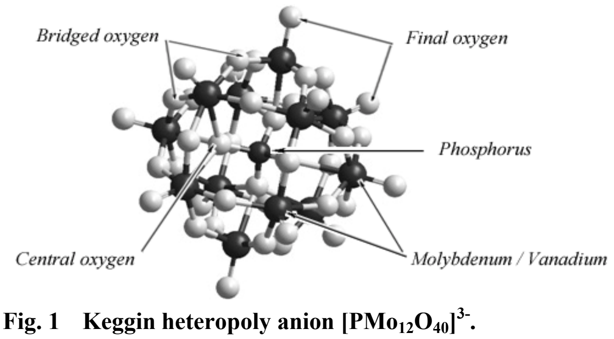
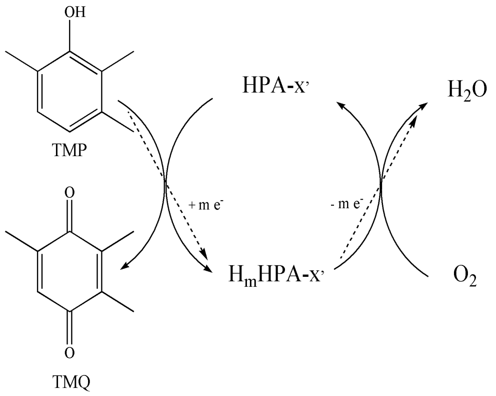


Fig. 1 Keggin heteropoly anion $[PMo_{12}O_{40}]^{3-}$.

the catalytic cycle. All physicochemical properties of the homogeneous catalysts based on HPA-*x'* solutions continuously alter during these redox processes [29]. Herewith, in the course of reaction (1) the redox potential E reaches its minimum and pH of catalyst solution attains its maximum. Electrons are transferred from the substrate molecule onto the HPA-*x'* molecule, that is equivalent to the reduction of m V^{V} atoms in HPA-*x'* to V^{IV}. In the course of reaction (2), the reverse situation is observed, electrons being transferred from the HPA-*x'* molecule into the oxygen one. In these processes, vanadium atoms undergo redox conversions ($V^{V} \leftrightarrow V^{IV}$), while HPA-*x'* solutions act as reversible oxidants.

Reaction (1) is usually carried out in mild conditions (40-60 °C). On the other hand, for a sufficiently rapid oxidation of the reduced form of catalyst via reaction (2), it has to be carried out at rather hard conditions (150-170 °C). Therefore, it is preferable to carry out these stages in separate reactors in order to obtain maximum selectivity. The catalytic process is illustrated by Scheme 1.



Scheme 1 TMP oxidation to TMQ assisted by the aqueous non-Keggin-type HPA-*x'* solutions.

2. Experiments

2.1 Chemicals and Catalysts

In all experiments, the authors used 95% 2,3,6-trimethylphenol purchased from "Aldrich Chemical Company" without additional purification. All organic solvents purchased from "Sibreakhim" (Novosibirsk) had the purity ≥ 98% and were also used without preliminary distillation.

A series of non-Keggin-type HPA-6', -7', -8', -10', and -12' aqueous solutions with different content of vanadium were synthesized from the stoichiometric amounts of V_2O_5, MoO_3, H_2O_2 and H_3PO_4 according to the method described in detail elsewhere [27].

Synthesis was performed in two stages. At the first stage, V_2O_5 was dissolved in a cold diluted H_2O_2 solution yielding a dark-red solution of peroxy vanadium compounds. On heating to room temperature thus obtained solution decomposed evolving O_2, giving an orange (~0.0125 M) solution of decavanadic acid $H_6V_{10}O_{28}$. The latter was immediately stabilized by the excess of H_3PO_4, producing a dark brown $H_9PV_{14}O_{42}$ aqueous solution with pH = 1.5 (Eqs. (4) and (5)) [31]. The second stage was performed by boiling according to reaction (6). The solution of $H_9PV_{14}O_{42}$ + H_3PO_4 obtained at the first stage was gradually added to the boiling suspension of MoO_3 + H_3PO_4 on stirring. MoO_3 slowly dissolved, yield is a homogeneous HPA-*x'* solution of desired composition. Thus obtained solution was evaporated to a required volume and filtered to check the completeness of the components dissolving. The initial pH and redox potential E_0 values of the solutions ranged within -0.06-(-0.11) and 1.008-1.064 V, respectively.

After synthesis the solutions obtained were characterized by ^{51}V and ^{31}P NMR. According to the spectra, Mo-V-P HPA-*x* (HPA-*x'*) solutions are not the solutions of individual compounds. In common case, the HPA-*x'* solutions are the complex equilibrium mixtures containing a set of Keggin- type HP- anions

$$V_2O_5 \xrightarrow{+\text{ cooled } H_2O_2} VO(O_2)^+ + \text{peroxy anions of } V^V \xrightarrow[-\ O_2]{} H_6V_{10}O_{28} \tag{4}$$

$$1.4\ H_6V_{10}O_{28} + H_3PO_4 \rightleftarrows H_9PV_{14}O_{42} + 1.2\ H_2O \tag{5}$$

$$(12 - x)\ MoO_3 + (1 - {}^{x}/_{14})\ H_3PO_4 + {}^{x}/_{14}\ H_9PV_{14}O_{42} + {}^{2x}/_{7}\ H_2O \longrightarrow H_{3+x}PMo_{12-x}V_{x'}O_{40} \tag{6}$$

with the different number of vanadium atoms, H^+-ions, cations VO_2^+, phosphoric acid and the products of their interaction. It should be noted that the NMR spectra of HPA-*x* and HPA-*x'* solutions are practically similar. This suggests that the solutions of both types contain the same particle sets. However, in the high-vanadium HPA-*x'* solutions having high concentration of phosphorus, concentration of free cations VO_2^+ proves to be lower than that in the solutions of Keggin-type HPA-*x*. These spectra are in detail described elsewhere [27].

2.2 Catalytic Reaction

The TMP oxidation reaction was studied in a thermostatic glass reactor (volume 100 mL) with a backflow condenser under atmospheric pressure in a two-phase system: aqueous HPA-*x'* solution/substrate dissolved in a definite OS (organic solvent). Weighted TMP (0.194 ÷ 1.224 g) was dissolved in OS (10 mL), and the solution obtained was introduced (entirely or by portions) into reactor with a certain amount of a thermostatic HPA-*x'* solution (50 mL). Reaction (1) was performed under mixing with magnetic stirrer in air at 20-60 °C for 10-30 min. After reaction completion, the two phases were separated in a funnel. If necessary, the product traces were extracted from the aqueous phase by chloroform (5 mL). The organic phase sample, containing reaction product, was analyzed with the gas-liquid chromatography (GLC method). In some experiments (specially noted) before reaction the catalyst solution was reduced by the 10 mol/L solution of hydrazine hydrate $N_2H_4 \cdot H_2O$ (which decomposes with a release of N_2) at 60-70 °C for 10-15 min (gradual introduction under stirring). The aqueous solution of reduced HPA-*x'* was regenerated by oxygen and used in the next catalytic cycle.

2.3 Catalyst Regeneration

Reduced HPA-*x'* solutions (H_mHPA-*x'*) were regenerated by oxygen in a thermostatic stainless steel autoclave, equipped with a backflow condenser, according to reaction (2). For the purpose a glass beaker with the H_mHPA-*x'* solution was put into the autoclave, the latter was closed, installed on magnetic stirrer, heated up to 170 °C and thermostated in 5-7 min without oxygen supply and stirring. After that, stirring was initiated simultaneously with oxygen (or air) supply through the metal capillary under certain pressure. Regeneration was performed for 15-20 min, the partial oxygen pressure P_{O_2} being 4 atm [30]. Regenerated catalysts were many times used in reaction (1).

2.4 Techniques

Redox potential *E* and pH of HPA-*x'* solutions before and after reaction (1) were measured at room temperature by the pH-meter "inoLab pH 730" from WTW. For pH registering, a combined pH-Electrode "Sen tix 41" preliminarily calibrated by buffers from WTW with pH = 4.01 and pH = 7.00 at 25 °C was used. For potential measurement, the authors used a platinum electrode "Sen tix ORP". Potential constancy of HPA-*x'* solution was attained in 1 min with an accuracy of ±0.001 V; pH constancy was attained in 2-3 min with an accuracy of ±0.01 pH units.

The ^{51}V and ^{31}P NMR spectra of HPA-*x'* solutions were recorded on a Bruker AVANCE 400 spectrometer at 105.24 MHz and 162.0 MHz, respectively, with $VOCl_3$ and 85% H_3PO_4 as external standards.

Substrate conversion and product amount were determined by the GLC-FID (gas chromatography with flame ionization detector) method using a HROMOS GH-1000 chromatograph with a capillary column St-WAX. Thermal programming was performed in the range of 140 °C-3 min-5 °C/min-170 °C (initial temperature of column 140 °C was kept during 3 min; after that the temperature was increased up to 170 °C with a heat rate of 5 °C/min). Tetramethyl-1,4-benzoquinone (DQ) purchased from "Merck-Schuchardt" had a purity 99.9% and was used as an internal standard. Chromatograms of patterns were registered and analysed with software "Hromos".

Relative error of chromatographic analysis was ±0.2%.

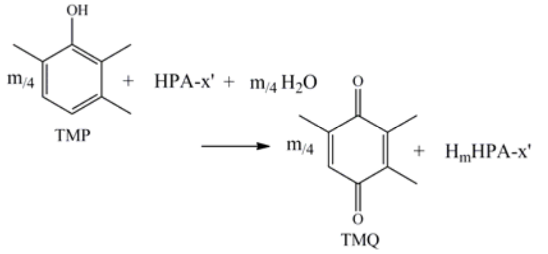
The TMQ yield (η) was calculated according to chromatographic data via Eq. (7).

$$\eta = \frac{k_0 \cdot k \cdot C \cdot V}{k_1 \cdot p \cdot m} \tag{7}$$

Here k_0 is a calibration factor, which is equal to the ratio of TMQ peak area to DQ peak area on chromatogram of solution with equal TMQ and DQ concentrations; k is a dimensionless value equal to the ratio of TMQ peak area to DQ peak area on sample chromatogram; C is the concentration of standard DQ solution (20 mg/mL); V is the volume of organic phase; k_1 is the purity degree of TMP (0.95); p is the ratio of organic phase volume to the standard DQ solution volume (both taken for analysis); m is the theoretical TMQ yield (g). The mean square error of η calculation via Eq. (7) is ±0.8%.

3. Results

The catalytic oxidation of TMP to TMQ in the presence of HPA-*x'* solutions may be presented by (Eq. (8)). Reaction was performed in the two-phase system.



(8)

It has been found that many factors influence both catalyst activity and desired product yield, such as the OS type, reaction temperature, content of vanadium (V) (the number of vanadium atoms in the HPA-*x'* composition (*x'*)), molar HPA-*x'*: substrate ratio, as well as redox potential E_o and catalyst solution pH.

The TMQ yield appears to be strongly dependent on the type of OS. The authors have tried six main solvent types such as aromatics, alcohols, carbonic acids, ethers, esters and ketones (Table 1 for the results obtained). It can be seen from the Table 1 when non-polar or weakly polar solvent is substituted by the polar one, the TMQ yield increases from ~20% to 99%. Halogen substituted and aromatic hydrocarbons are inefficient as OS (cycles 1-3). TMQ yield appears to decrease in the series: alcohols > n-carboxylic acids > esters, ketones > ethers > hydrocarbons. Among alcohols the primary alcohols were found to be the most efficient. The secondary and especially tertiary alcohols are partially dehydrated by the HPA-*x'* solutions (strong Brønsted acids) into the corresponding olefins, and therefore are not good for the system. More detailed studies have shown that carbon chain branching in primary alcohols also noticeably worsens the TMQ yield. Therefore, the primary normal alcohols, containing from 6 to 9 carbon atoms, are the most appropriate as organic solvents (Fig. 2). It should be noted that all mentioned in the table cycles were carried out at the same sample of catalyst.

The authors have also studied the TMQ yield dependence on reaction temperature. At temperature below 40 °C, the TMQ yield decreases (η < 99%), and reaction time *t* essentially increases (Table 2). At temperatures 40 °C and 60 °C, the authors obtained similar η values, however, at 60 °C reaction time was twice shorter. Therefore, the authors have chosen reaction temperature 60 °C as the most optimum, providing the best ratio between the TMQ yield and reaction time. All results mentioned in Table 2 also were obtained at the same sample of catalyst.

Then the authors have studied how the TMQ yield

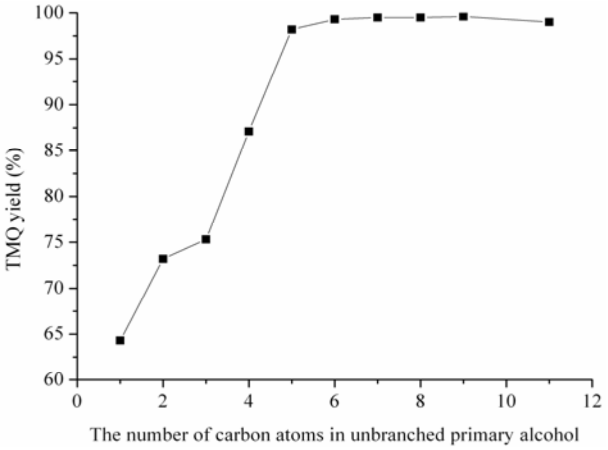


Fig. 2 TMQ yield versus the number of carbon atoms in the primary non-branched alcohol.

Table 1 TMQ yield versus organic solvent type in the two-phase "water-OS" system in the presence of the 0.3 M HPA-7' solution[a].

Cycle	Solvent	Structural formula	TMQ yield (mass %)
1	Benzene	C_6H_6	24.5
2	Carbon tetrachloride	CCl_4	20.5
3	Chloroform	$CHCl_3$	22.0
4	Ethyl benzoate	C_2H_5-O-CO-C_6H_5	61.3
5	Phenyl acetate	C_6H_5-O-CO-CH_3	polymerization of solvent
6	N-Amyl acetate	CH_3-CO-O-*n*-C_5H_{11}	65.2
7	Pentoxy pentane	*n*-C_5H_{11}-O-*n*-C_5H_{11}	40.1
8	Methoxy octan	*n*-C_8H_{17}-O-CH_3	53.4
9	Diphenyl ether	$(C_6H_5)_2O$	60.0
10	5-nonanone	C_4H_9-CO-C_4H_9	62.3
11	2-oktanone	n-C_6H_{13}-CO-CH_3	64.7
12	6-undecanone	n-C_5H_{11}-CO-n-C_5H_{11}	53.9
13	Hexanoic acid	$C_5H_{11}COOH$	67.3
14	Heptanoic acid	$C_6H_{13}COOH$	66.8
15	Octanoic acid	$C_7H_{15}COOH$	66.6
16	Tridecanoic acid (T_{Mp} = 41-42 °C)	$C_{12}H_{25}COOH$	65.0
17	1- butanol	C_4H_9OH	87.0
18	T- butanol	$(CH_3)_3COH$	78.0
19	1-pentanol	$C_5H_{11}OH$	96.1
21	3-pentanol	$(CH_3CH_2)_2CHOH$	88.3
22	2,2-dimethyl-1-propanol	$(CH_3)_3CCH_2OH$	91.5
23	1-hexanol	$C_6H_{13}OH$	99.0
24	2-hexanol	$CH_3(CH_2)_3CHOHCH_3$	87.0
25	1-heptanol	$C_7H_{15}OH$	98.5
26	1-octanol	$C_8H_{17}OH$	99.0
27	2-octanol	$CH_3(CH_2)_5CHOHCH_3$	88.5
28	2-ethyl-1-hexanol	$CH_3(CH_2)_3CH(CH_2CH_3)CH_2OH$	90.0
29	1-nonanol	$C_9H_{19}OH$	98.7
30	1-undecanol (T_{mp} = 19 °C)	$C_{11}H_{23}OH$	98.2

[a] 50 mL 0.3 M $H_9P_2Mo_9V_{7'}O_{54}$ (HPA-7') solution, 0.408 g TMP, 60 °C, air atmosphere, t = 25 min (100% TMP conversion), molar HPA-7':TMP ratio = 5. Weighted TMP was dissolved in 10 mL of organic solvent and immediately introduced into the HPA-7' solution. All experiments were carried out at the same sample of catalyst, which after each cycle was regenerated according to reaction (2) and once again used in the process (30 cycles in total).

Table 2 Reaction temperature influence on the TMQ yield and TMP conversion time in the presence of the 0.3 M HPA-8' solution[a].

Cycle	Temperature (°C)	Reaction time (min)	TMQ yield (mass %)
1	20	210	98.7
2	30	55	98.8
3[b]	40	30	99.4
4	40	30	99.6
5	60	15	99.5
6	60	15	99.4

[a] 50 mL 0.3 M $H_{14}P_2Mo_{10}V_{8'}O_{62}$ (HPA-8') solution, 0.408 g TMP, air atmosphere, 100% TMP conversion, molar HPA-8':TMP ratio = 5, 10 mL octanol-1. The solution of catalyst after each cycle was regenerated according to reaction (2) and then once again used in the process (six cycles in total);

[b] The reaction was performed in an argon atmosphere.

Table 3 Molar HPA-8’:TMP ratio influence on the TMQ yield and reaction time in the presence of the 0.2 M HPA-8’ solution[a].

Cycle	TMP sample (g)	HPA-8’:TMP molar ratio	TMQ yield (mass %)	Reaction time (min)
1[b]	0.272	5	98.7	15
2	0.340	4	98.8	15
3	0.453	3	89.9	20
4	0.272	5	98.6	15
5	0.194	7	98.8	10

[a] 50 mL 0.2 M $H_{14}P_2Mo_{10}V_8{\cdot}O_{62}$ (HPA-8’) solution, 60 °C, air atmosphere, 100% TMP conversion, 10 mL octanol-1. After each cycle the catalyst was regenerated according to reaction (2) and reused (five cycles in total);

[b] The reaction was performed in an argon atmosphere.

Table 4 TMQ yield versus V^V concentration in the HPA-7’ solution[a].

HPA-7’ concentration (mol·L^{-1})	V^V concentration (mol·L^{-1})	HPA-7’:TMP molar ratio	TMQ yield (mass %)
0.06	0.4	1.2	57.5
0.11	0.8	2.2	70.0
0.17	1.2	3.4	82.3
0.23	1.6	4.6	95.0
0.24	1.7	4.8	98.0
0.26	1.8	5.2	98.8
0.29	2.0	5.8	99.4
0.34	2.4	6.8	99.2

[a] 50 mL $H_9P_2Mo_9V_7{\cdot}O_{54}$ (HPA-7’) solution, 0.341 g TMP, 60 °C, air atmosphere, $t = 15$ min (100% TMP conversion), 10 mL hexanol-1. After each cycle catalyst was regenerated according to reaction (2). Regenerated catalyst (starting from [HPA-7’] = 0.06 M) was concentrated to obtain higher concentration and used in the next cycle.

depends on the molar HPA-x’:TMP ratio using the 0.2 M HPA-8’ solution (Table 3 for the results obtained). Data analysis shows that balance between the TMQ yield and reaction time is the best, when the molar HPA-8’:TMP ratio ranges from 4 to 5. When this ratio exceeds value 5, the total TMP conversion time decreases (cycle 5), η remaining the same. Therefore, the molar HPA-8’:TMP ratio equaling 5 is the most appropriate, because it allows to achieve the optimal balance between the TMQ yield and reaction time without extra catalyst spending.

The catalytic activity of HPA-*x’* solution depends on its concentration and the number of vanadium atoms in HPA-*x’* molecule (*x’*). The authors have found that the TMQ yield exceeds 99%, when the concentration of V^V in the solution of HPA-7’ (Table 4) is higher than 1.8 M (Fig. 3). The value of concentration determines the minimum necessary concentration of the HPA-*x’* solutions. Thus for HPA-7’ the necessary concentration of V^V is obtained in 0.25 M solution, while in the case of HPA-8’ the 0.2 M solution is enough.

In order to study the stability of the catalytic systems the authors have also performed the many-cycle tests of three catalytic systems (HPA-6’ + OS, HPA-10’ + OS, HPA-12’ + OS) subject to already obtained parameters for determining the optimal characteristics of the catalyst solutions (Tables 5-7 for the results obtained). According to Table 5, for the system HPA-6’ + OS the desired product yield 99.0%-99.5% is attained in the

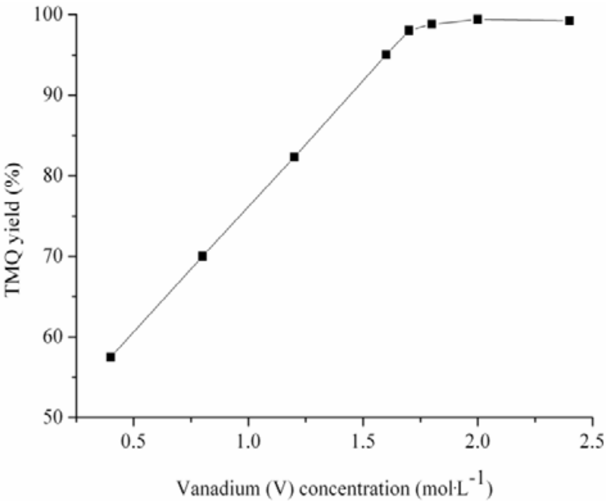


Fig. 3 TMQ yield versus V^V concentration in the HPA-*x’* solution.

Table 5 TMQ yield dependence on the parameters of catalytic system HPA-6’ + OS in many-cycled tests[a].

Cycle	HPA-6’ concentration ($mol{\cdot}L^{-1}$)	Solvent	HPA-6’:TMP molar ratio	pH_0	E_0 (V)	TMQ yield (mass %)
1	0.3	1-octanol	5	-0.06	1.008	87.6
2	0.3	1-octanol	5	0.09	1.009	98.8
3	0.3	1-heptanol	5	0.24	0.968	99.4
4	0.3	1-hexanol	5	0.32	0.953	99.4
5	0.3	1-heptanol	5	0.33	0.948	98.1
6	0.3	1-heptanol	5	0.20	0.973	99.3
7	0.3	1-heptanol	5	0.27	0.961	99.3
8	0.3	1-heptanol[b]	5	0.31	0.949	99.2
9	0.35	1-heptanol	5.8	0.16	0.974	99.1
10	0.35	1-heptanol	5.8	0.18	0.961	99.5
11[c]	0.35	1-heptanol	2.9	0.19	0.959	94.7

[a] 50 mL $H_6P_2Mo_9V_6{\cdot}O_{50}$ (HPA-6’) solution, 0.408 g TMP, 60 °C, air atmosphere, $t = 20$ min (100% TMP conversion). Weighted TMP was dissolved in 10 mL of organic solvent and immediately introduced into the HPA-6’ solution. After each cycle catalyst was regenerated according reaction (2) and reused (in cycles 1-8 and 9-11);

[b] 5 mL heptanol-1;

[c] TMP was introduced by two portions 0.408 g each, time interval being 20 min.

Table 6 TMQ yield dependence on the parameters of catalytic system HPA-10’ + OS in many-cycled tests[a].

Cycle	Solvent	pH_0	E_0 (V)	TMQ yield (mass %)
1[b]	1-heptanol	-0.11	1.053	90.7
2	1-heptanol	0.09	0.985	99.5
3	1-heptanol	0.28	0.933	99.6
4	1-heptanol	0.51	0.885	90.5
5	1-hexanol	0.43	0.904	98.8
6	1-hexanol	0.37	0.915	99.2

[a] 50 mL 0.2 M $H_{17}P_3Mo_{16}V_{10}{\cdot}O_{89}$ (HPA-10’) solution, 0.408 g TMP, 60 °C, air atmosphere, $t = 20$ min (100% TMP conversion), molar HPA-10’:TMP ratio = 3.33. Weighted TMP was dissolved in 10 mL of OS and immediately introduced into the HPA-10’ solution. After each cycle catalyst was regenerated according reaction (2) and used in six cycles;

[b] Fresh catalyst solution ($pH_0 = -0.13$, $E_0 = 1.093$ V) was pre-reduced by $m = 1$ e^- with 10 M solution of $N_2H_4{\cdot}xH_2O$.

Table 7 TMQ yield dependence on the parameters of catalytic system HPA-12’ + OS in many-cycled tests [a].

Cycle	TMP sample (g)	HPA-12’/TMP molar ratio	Solvent (mL)	pH_0	E_0 (V)	E_{fin} (V)	t (min)	TMQ yield (mass %)
1[b]	0.408	3.33	1-hexanol (10)	0.12	0.979	0.917	20	99.4
2	0.408	3.33	1-hexanol (10)	0.31	0.938	0.876	20	99.6
3	0.408	3.33	1-hexanol (10)	0.46	0.896	0.832	20	97.9
4	0.408	3.33	1-hexanol (10)	0.36	0.919	0.854	20	99.5
5[c]	0.816	1.67	1-hexanol (15)	0.31	0.938	0.834	40	98.0
6[d]	0.816	1.67	1-hexanol (15)	0.41	0.914	0.794	30	97.6
7[e]	1.224	1.11	1-hexanol (15)	0.33	0.928	0.769	40	91.9
8	0.408	3.33	1-octanol (10)	0.38	0.923	0.860	20	99.4
9[d]	0.816	1.67	1-octanol (15)	0.37	0.924	0.816	30	96.6
10[d]	0.816	1.67	1-octanol (15)	0.36	0.925	0.822	30	97.3
11[d]	0.816	1.67	1-heptanol (15)	0.31	0.934	0.836	30	97.2

[a] 50 mL 0.2 M $H_{19}P_3Mo_{14}V_{12}{\cdot}O_{89}$ (HPA-12’) solution, 60 °C, air atmosphere, 100% TMP conversion. After each cycle catalyst was regenerated according to reaction (2) and reused (10 cycles in total). Regeneration conditions starting from the second cycle: 140 °C, $P_{O_2} = 4$ atm, regeneration time 30 min;

[b] Fresh catalyst solution ($pH_0 = -0.08$, $E_0 = 1.064$ V) before experiment was reduced by $m = 2.8$ e^- with 10 M solution of $N_2H_4{\cdot}H_2O$. Catalyst regeneration at 170 °C provided a small amount of precipitate;

[c] TMP was introduced by two portions 0.408 g each, time interval being 20 min. 1 mL of 30% H_2O_2 solution was added with the second portion;

[d] TMP was introduced by two portions 0.408 g each. Second portion was added in 10 min with 1 mL of 30% H_2O_2 solution;

[e] TMP was introduced by three portions 0.408 g each. Second and third portions were introduced in 10 min, both with 1 mL of 30% H_2O_2 solution.

presence of 0.3-0.35 M HPA-6' solution, the molar HPA-6':TMP ratio being 5.0-5.8. At the same time initial redox potential and catalyst solution pH are varied within E_0 = 0.949 ÷ 0.991 V and pH_0 = 0.13 ÷ 0.32, respectively. During all cycles, catalyst remained stable and retained its homogeneity. Note (Table 5, cycle 8) that a two-fold reduction of organic solvent volume (to 5 mL) did not reduce value η. In alcohols C_6-C_8 the values of TMQ yield were close.

It is well known that non-reduced HPA solutions are the strong Brønsted acids, and their first three protons are completely dissociated [19, 32]. Evidently (Table 5) the high acidity of HPA solutions has a negative effect on the desired product yield (cycle 1). Therefore, if pH of synthesized solution or HPA-*x'* solution after regeneration is below 0, then catalyst solution should be partially reduced before reaction (1). It results in increasing the catalyst pH and obtaining higher TMQ yield already at the first cycle.

In system HPA-10' + OS the TMQ yield exceeds 99% in the presence of 0.2 M HPA-10' solution at E_0 = 0.907 ÷ 0.985 V and pH_0 = 0.07 ÷ 0.40 (Table 6 for the results obtained). Note that in going from HPA-6' to high-vanadium HPA-10' the optimal molar HPA-*x'*:TMP ratio decreases from 5 to 3.33. As can be seen from the table the catalyst remains stable and retains its homogeneity in reaction course at least in six cycles. In the presence of alcohols C_6-C_7 the TMQ yield values are similar. Note also that a too low solution redox potential before experiment 4 (Table 6) causes the decrease of TMQ yield (values pH_0 and E_0 of HPA-10' before reaction correspond to HPA reduction by m = 4.4 electrons). At the same time the reduction of 0.2 M HPA-10' by m = 1 e^- before the first cycle is not enough, since pH value remains below 0, and so the TMQ yield decreases (cycle 1).

Studying the system HPA-12' + OS, the authors have obtained the TMQ yield higher than 99% at the following system parameters: the molar HPA-12':TMP ratio 3.33, initial potential E_0 = 0.911 ÷ 0.980 V and pH_0 = 0.12 ÷ 0.40. Before the first cycle 0.2 M HPA-12' solution was reduced by m = 2.8 e^-, and it was enough for the TMQ yield to exceed 99% at the first cycle already (Table 7). According to data analysis, the redox potential of catalyst solution after regeneration (i.e., initial value E_0 in the next cycle) and the rate of its decrease in the next cycle have significant influence on value η. In experiments, when the E value after regeneration was below 0.911 V, the TMQ yield in the next cycle was noticeably lower. This evidences that high initial potential of HPA-*x'* solution and the optimum molar HPA-*x'*:TMP ratio is the obligatory criteria for obtaining η higher than 99%. Nevertheless the authors have found that the 0.2 M HPA-12' solution is not the optimal one. The reason is that during its regeneration at elevated temperature (170 °C) after the first cycle, a precipitate was produced, which was the mixture of oxides of V^V and V^{IV}. This required catalyst solution substitution by the fresh one and the decrease of catalyst regeneration temperature. As a consequence, it leaded to the increase of both catalyst regeneration time and total catalytic cycle time.

4. Discussion

Systems providing low TMQ yield have been analyzed by the GLC and the GC-MS methods. According to analysis, BP (2,2',3,3',6,6'-hexamethyl-1,4'-bisphenol) and PP (2,3,6-trimethyl-4-(2',3',6'-trimethyl-phenoxyphenol) are the main side products. There are also tars of unidentified composition in trace amount. Therefore, it has been necessary to find the appropriate parameters of reaction (1) in order to provide the higher TMQ yield and to reduce the rate of side reactions.

According to analysis of data obtained, it is possible to accelerate target reaction (1) by increasing catalyst activity and by choosing the optimal molar HPA-*x'*:Su ratio. At the same time, the catalytic activity of HPA-*x'* solution depends on its total concentration and the number of vanadium atoms in it. As shown for achieving the TMQ yield higher than 99%, it is necessary to use HPA-*x'* in excess, with $[V^V]$ being ≥

1.8 M in solution.

Catalyst redox potential E before reaction seems to be also of key importance for reaction (1). According to the data obtained, the higher E before reaction (1) is and the slower it decreases in the reaction course, the higher the TMQ yield is. Initial E, in its turn, depends on catalyst composition (the number of vanadium atoms in HPA-*x'*) and concentration. If electrons are not fast enough transferred into the HPA-*x'* molecules (in case when initial catalyst potential E_0 is not high enough), TMQ yield is low, and side products form.

It should be noted that in going from HPA-6', -7', -8' to high-vanadium HPA-10' and HPA-12', the optimum molar HPA-*x'*:TMP ratio decreases from 5 to 3.33. This effect may be explained as follows. If concentration of V^V is high (HPA-10' and HPA-12'), initial redox potential of such solutions is also higher, its value decreasing slower in the reaction (1). Therefore, TMQ yield is the higher and the larger is *x'* (the number of vanadium atoms in HPA-*x'*).

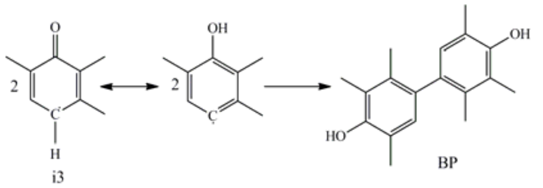
It was shown by certain studies (cycles 1 and 3 in Tables 3 and 4, accordingly) that high TMQ yield is preserved, when air is substituted by argon in the reaction (1). This fact proves that in this catalytic system oxygen used for substrate oxidation origins from water molecules.

Two observations such as TMQ yield dependence on the catalyst redox potential and on the rate of electron transfer, as well as experimental detection of side products with C-C and C-O combinations (which are typical only for phenols oxidation through phenoxyl radicals), allow one to suggest that TMP to TMQ oxidation in the HPA-*x'* solutions goes through several elementary stages. These stages involve a stepwise elimination of two protons and the transfer of four electrons from the TMP molecule with a hydrolysis of intermediate carbocation (Scheme 2). According to the Scheme 2, several highly reactive particles are formed, when TMP is converted to TMQ. These particles are radicals (i2, i3, i6) and carbocation i4. If electron transfers into the HPA-*x'* molecule is not fast enough, these particles may recombine or react with non-radical particles, yielding various side products. The authors have failed to register such particles directly in reaction solution by NMR and EPR (electron paramagnetic resonance) spectroscopy, however, all experimental data well agree with the presented scheme. Thus, BP and PP (the main side products) may be generated due to recombination of two free radicals according to Eqs. (9) and (10).

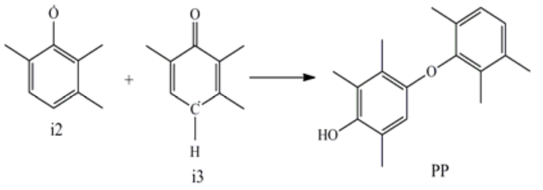
It is possible to decelerate the recombination reactions by decreasing radicals' diffusion rate (their mobility), e.g., by increasing the solvent viscosity. Another approach is to create the dense solvate shells around radical particles, thus ensuring the activation energy appearance (this activation energy is equal to salvation heat). The authors have found that the TMQ yield depends on the nature of organic solvent, i.e., it decreases in going from polar solvents to the non-polar ones. Most likely, non-polar solvents badly solvate the reactive centers of intermediate particles. The type of solvent capable of appropriate solvation depends on the nature of reactive center, which is to be blocked out. According to the Scheme 2, the appropriate solvent should solvate two types of reactive centers simultaneously: (1) oxygen atom in particles i2, i6; (2) carbon atom of particle i3 in position 4. Primary alcohols with non-branched carbon chain with six to nine carbons appear to be the best for the purpose. Moreover, since these alcohols do not mix with water, the authors consider that they provide an orienting effect, positioning the OH-groups of substrate molecules along the boundary between the phases in the maximum closeness to the oxidizer (HPA-*x'*).

Another important property of n-alcohol (beside viscosity) is its boiling temperature, since it should differ from the boiling temperature of TMQ (T_{bp} = 215.3 °C) at least by 10-15 °C for easier product separation from the solvent. With this regard, octanol-1 (T_{bp} = 195 °C) seems to be the best among the chosen alcohols. It was shown by the GLC method that in spite of significant HPA-*x'* excess with respect to TMP, the degree of solvent decomposition does not exceed 3% of its total volume due to the high rate of reaction (1).

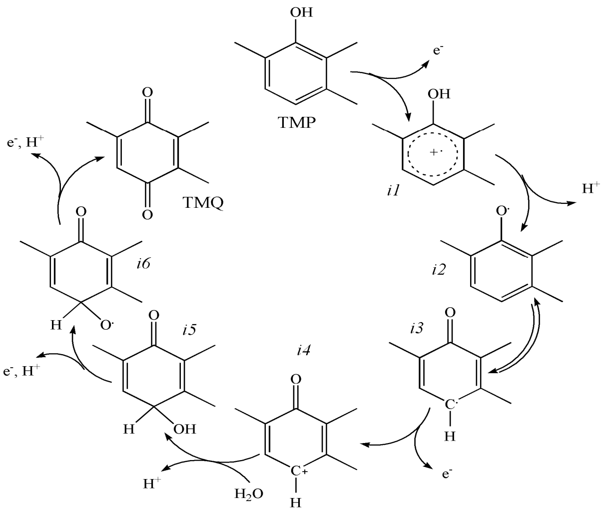
It has been found that if large TMP amount is immediately introduced into the catalyst solution with low initial *E*, the TMQ yield decreases. Most likely, this happens due to the excess radical generation. Because of low *E* value, the excess radicals are not able to give remaining electrons onto HPA-*x'*. Therefore, they interact with other particles present in the solution, yielding dimers and high molecular compounds (tars). In order to reduce the tar formation, it is necessary to decrease the instant TMP concentration in the reaction mixture. Therefore, TMP should be introduced by small portions in definite time intervals. It is necessary that instant molar HPA-*x'*:TMP ratio for HPA-10' and HPA-12' should not be less than 3.33, and that for HPA-6', -7', -8' should not be less than 5.0. Moreover, since the increasing load on the catalyst deepens its reduction (low potential E_{fin}), it is better to use HPA-*x'* with higher vanadium content, as their potential decreases slower in the course of reaction (1). Following all above described conditions one may improve both TMQ yield and process productivity. It is important to understand that although HPA-*x'* is taken in excess relative to Su, the catalyst is stable and is used for a long time (several months) in many cycles of TMP oxidation into TMQ. After regeneration it restores its properties, remaining homogeneous.



(9)

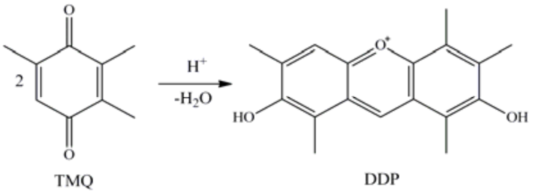


(10)



Scheme 2 Mechanism of TMP to TMQ oxidation in the presence of modified non-Keggin-type HPA-*x'* solutions.

It has been found that if pH of the synthesized catalyst solution at the first cycle is below zero, the TMQ yield decreases. Probably this effect is caused by the formation of DDP (dioxidibenzopyrilium), which is a water soluble product of acid-base TMQ dimerization (Eq. (11)).



(11)

It is possible to suppress this side reaction by decreasing the HPA-*x'* solution acidity via its partial reduction with the 10 M solution of hydrazine hydrate $N_2H_4 \cdot xH_2O$ before the first cycle. It has been found that 0.3 M HPA-6' solution is rather to be reduced by m = 1.6 e^-, 0.2 M HPA-10' solution—by m = 2.7 e^-, and 0.2 M HPA-12' solution—by m = 2.8 e^-.

Analyzing all above described regularities, the authors may conclude that 0.2 M HPA-10' solution is the most appropriate catalyst for the studied reaction, since it requires less ratio catalyst:substrate than HPA-6', -7', -8' solutions. Moreover, as the load on this catalyst increases, its redox potential decreases slower than that of other solutions. This provides higher productivity and prevents side products formation, when less than four electrons are transferred from the TMP molecule. The authors established that initial potential of catalyst solution should range within $0.907 \le E_0 \le 0.985$ V, and its pH should range from

0.07 to 0.37. Potential close to the upper limit ($E_0 \approx$ 0.985 V) is the most preferable, since it allows to support high potential during the catalytic reaction and provides the maximal catalyst productivity. Concentration 0.2 M seems to be optimal, since it fits condition $[V^V] \geq 1.8$ M on one hand, and allows to retain the hydrolytic stability of HPA-10' solution in case of its concentrating on the other hand.

5. Conclusions

The catalytic oxidation of 2,3,6-trimethylphenol to 2,3,5-trimethyl-1,4-benzoquinone was investigated in the two-phase system at 20-60 °C under atmospheric pressure in the presence of non-Keggin-type aqueous solutions of Mo-V-phosphoric heteropoly acids. The reaction was found to go via the radical mechanism, which provides a stepwise elimination of two protons, and is accompanied by the transfer of four electrons from the TMP molecule on the oxidant. At the same time, this process produces several highly reactive particles such as radicals (i2, i3, i6) and carbocation i4. If electron transfers into the HPA-*x'* molecules is not fast enough, these intermediate particles may recombine yielding various side products. It has been shown that it is possible to decelerate the side reactions and to increase the desired product yield by using the high molar HPA-*x'*:TMP ratio and providing $[V^V] \geq$ 1.8 M in the HPA-*x'* solutions. The HPA-*x'* solutions with high vanadium content are proved to be the best for TMP oxidation, since they have high initial redox potential, which decreases slowly in the reaction course. In this case, electron transfer from TMP into the catalyst is fast, and the life time of highly reactive intermediate particles shortens considerably, preventing their recombination.

The 0.2 M HPA-10' ($H_{17}P_3Mo_{16}V_{10'}O_{89}$) solution is proved to be the most efficient for the TMP oxidation. This solution is characterized by the high oxidative capacity, thermal stability and the high rate of regeneration at 170 °C. Moreover, owing to its high stability the HPA-10' solution can go through many times repeated redox conversions, and therefore may be used in many cycles for quite a long time. With this solution, the total TMP conversion is reached in 15 min at 60 °C, the molar HPA-10':TMP ratio being 3.33, and octanol-1 being used as organic solvent. Herewith, the TMQ yield attains more than 99%. The target reaction is performed in the two-phase system "water-organic solvent", which allows one to isolate reaction product from the catalyst simply by phase separation. Therefore, using new non-Keggin-type HPA-*x'* solution as catalyst one may synthesize TMQ with good productivity and high yield. Moreover, this process is environmentally friendlier in comparison with conventional industrial one going in the presence of aqueous $CuCl_2$, since it does not produce chlorinated quinones.

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