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Preparation of Vitamin K_3 in Mo–V–P Heteropoly Acid Solutions by Diene Synthesis

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Abstract—The possibility of obtaining vitamin K_3 (2-methyl-1,4-naphthoquinone, menadione) by diene synthesis from accessible substrates such as 2-methylphenol (*o*-cresol) and 2-methylaniline (*o*-toluidine) was shown. The bifunctional catalysts of these processes are the aqueous solutions of Mo–V–P heteropoly acids, which allow the oxidation and diene synthesis to be performed as a one-pot process.

Keywords: hydroquinone, naphthoquinones, heteropoly acids, oxidation, diene synthesis

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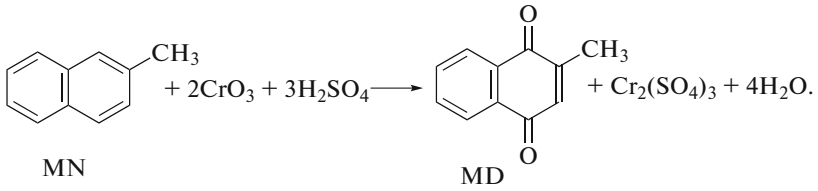
INTRODUCTION

2-Methyl-1,4-naphthoquinone (vitamin K_3, menadione, MD) is a fat-soluble vitamin of vitamin K group. It is necessary for the biosynthesis of prothrombin and other blood coagulation factors and is involved in bone tissue mineralization processes. Menadione is a parent compound for all K group vitamins: vicasol—a water-soluble (bisulfite) form of vitamin K_3—and vitamins K_4 and K_1 are obtained from it. MD in the form of vicasol is widely used in medicine for treatment of many diseases and in animal husbandry to increase the productivity of all types of animals [1]. The growing demand for K group vitamins has stimulated a search for effective methods for their synthesis.

Industrial Methods for the Synthesis of Vitamin K_3

The main method for the industrial production of MD is the noncatalytic oxidation of 2-methylnaphthalene (MN) with a chromium mixture by reaction (I) using a fivefold excess of CrO_3 [2].



MN MD (I)

The production of vitamin K_3 by this technology is not environmentally friendly because of the abundance of wastewater containing toxic chromium compounds, tar, and acids. The production is also uneconomical as the selectivity of the target reaction (I) is below 50%. 2-Methylnaphthalene is an inaccessible raw material: it is isolated from coal tar together with 1-methylnaphthalene, after which the desired isomer is separated by freezing.

Many other methods for the synthesis of menadione by oxidation of MN were proposed in addition to the above process [3–6], but all of them did not become more effective than the existing industrial method. Also, there are developments in which diene synthesis followed by the oxidation of adducts is used to obtain vitamin K_3 [7, 8]. The disadvantage of these methods is the multistage and environmentally nonfriendly process. Thus, in the patent [7], it was pro-

Abbreviations: MD, 2-methyl-1,4-naphthoquinone (vitamin K_3, menadione); MN, 2-methylnaphthalene; HPA, heteropoly acid; Su, substrate; *x*, the number of V atoms in the HPA; *m*, the degree of reduction of HPA-*x* equal to the number of accepted electrons or the number of V^{IV} ions; *E*, redox potential of the HPA-*x* solution; MBQ, 2-methyl-1,4-benzoquinone; DMSO, dimethyl sulfoxide; SHE, standard hydrogen electrode.

posed that vitamin K_3 be synthesized from 1-acetoxy-1,3-butadiene and 2-methyl-1,4-benzoquinone (toluquinone), forming a mixture of isomeric adducts with a yield of ~60%. The resulting adducts can be oxidized to menadione with either 30% nitric acid or a mixture of sodium nitrite and acetic acid at 50–60°C with a yield of ~80%. However, neither the starting diene nor quinone are ready-made industrial products, and they also need to be synthesized: diene is synthesized from crotonic aldehyde and acetic anhydride, and quinone is obtained by the oxidation of *o*-toluidine.

Synthesis of Menadione in Mo–V–P Heteropoly acid Solutions

In the search for new technologies for the production of menadione in the late 1990s, an original solution to this problem was proposed at Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences [9, 10]. The new low-waste technology for the synthesis of vitamin K_3, later called Vikasib (Siberian Vikasol), is based on the use of aqueous solutions of Mo–V–P heteropoly acids ($H_{3+x}PMo_{12-x}V_xO_{40}$, HPA-*x*, where *x* is the number of V atoms in HPA-*x*) as the catalysts of oxidation. In the new process, the oxidized substrate (Su) was 2-methylnaphthol-1, in contrast to 2-methylnaphthalene used in the industrial process.

The HPA-*x* solutions are used as selective catalysts of partial oxidation of various organic compounds with oxygen [11–19], occurring by the equation

$$\begin{gathered} m/2\,\mathrm{Su} + m/2\,\mathrm{H_2O} + \text{HPA-}x \\ \rightarrow m/2\,\mathrm{SuO} + \mathrm{H}_m\text{HPA-}x. \end{gathered} \quad \text{(II)}$$

It is very important for catalysis that the HPA-*x* solutions are characterized by *reversible oxidizability*; i.e., their reduced forms (H_mHPA-*x*, where *m* is the degree of reduction of HPA-*x* equal to the number of accepted electrons or the number of V^{IV} ions) are capable of being oxidized by molecular oxygen with regeneration of the initial form of HPA-*x* by the reaction

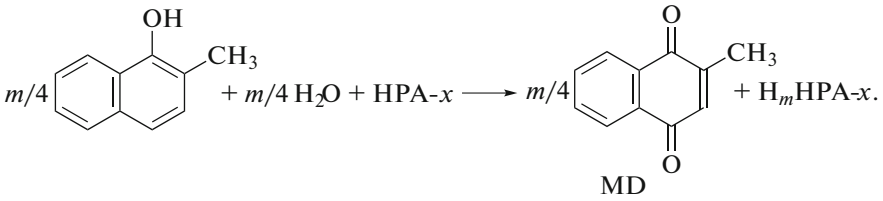
$$\mathrm{H}_m\text{HPA-}x + m/4\,\mathrm{O_2} \rightarrow \text{HPA-}x + m/2\,\mathrm{H_2O}. \quad \text{(III)}$$

Therefore, in the presence of HPA-*x* solutions, a unique opportunity to close the catalytic cycle of the two-stage oxidation (IV) of Su with oxygen appears, in which the reversibly acting oxidant (HPA-*x*) actually acts as a catalyst. Note that in Mo–V–P HPA-*x* solutions, only the vanadium atoms are involved in the redox transformations: $V^V \rightleftarrows V^{IV}$.

$$\mathrm{Su} + 1/2\,\mathrm{O_2} \xrightarrow{\text{HPA-}x} \mathrm{SuO}. \quad \text{(IV)}$$

The HPA-*x* solutions have high stability [20, 21]; therefore, the HPA-*x* solution regenerated by reaction (III) can be repeatedly used in the target reaction (II) in the second and subsequent cycles, including reactions (II) + (III).

The reversible oxidizability of HPA-*x* solutions (in contrast to CrO_3 used in industrial reaction (I)) became the main distinction of the new low-waste Vikasib technology [22]. Optimization of the process provided 90% selectivity of the oxidation of 2-methylnaphthol-1 to menadione by reaction (IIa).



(IIa)

The use of this technology in Russia, however, is limited by the shortage of raw materials because naphthol-1, from which 2-methylnaphthol-1 could be obtained by methylation [23], is not produced in Russia. Therefore, we sought for alternative methods for the synthesis of menadione from more accessible substrates in HPA-*x* solutions.

Previously, we showed that HPA-*x* solutions, which are strong Brönsted acids, are capable of exhibiting bifunctional (acid and oxidative) properties, catalyzing both diene syntheses and oxidations [16]. In HPA-*x* solutions in an atmosphere of 1,3-butadiene, 9,10-anthraquinone can be synthesized from 1,4-naphthoquinone or hydroquinone. In this case, the oxidation and Diels–Alder reaction proceed in one technological stage [16].

The present study shows that by combining the acid-catalyzed diene synthesis and oxidation in the presence of HPA-*x* solutions, it is possible to obtain menadione in one technological stage from 2-methylphenol (*o*-cresol) or 2-methylaniline (*o*-toluidine) in the presence of 1,3-butadiene.

EXPERIMENTAL

Menadione was synthesized by reaction (II) in a thermostatted two-necked 100 mL glass flask while stirring the reaction mixture with a magnetic stirrer in a 1,3-butadiene atmosphere. An exact sample of *o*-cresol or the calculated volume of *o*-toluidine was placed in the flask with a certain amount of 0.25 M HPA-*x* solution (the number of vanadium atoms *x* in HPA-*x* was varied). The flask was connected to a chamber filled

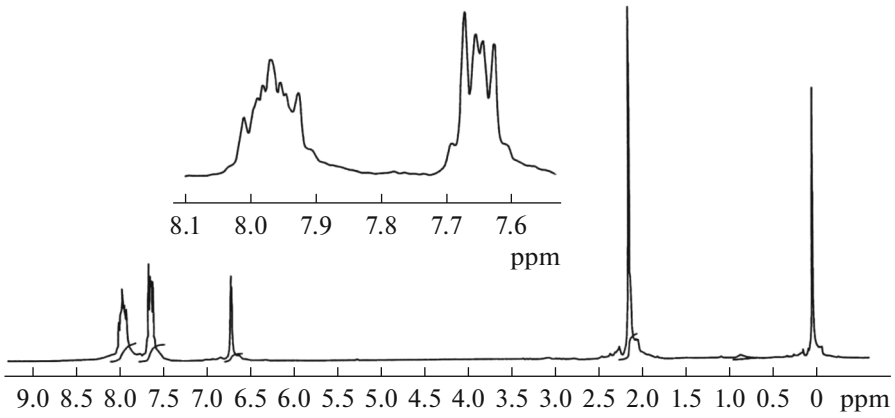


Fig. 1. ^{1}H NMR spectrum of the isolated menadione in CCl_4.

with 1,3-butadiene and blown through a long tube lowered to the solution surface; the second throat was closed, and the reaction was conducted at a given temperature (20–60°C). The reaction progress was monitored by GLC using a Khromos GKh-1000 chromatograph (Khromos, Russia; SE-Z0 type capillary column, thermal programming in the range 100–250°C).

The state of the catalyst was controlled by the procedure described in [20, 24], intermittently monitoring the decrease in the redox potential (E) of the HPA-x solution during the reaction. The reaction products were extracted with benzene or diethyl ether (3 × 20 mL), dried over calcium chloride, then the solvent was distilled off, and the residue was weighed. The choice of extractant made it possible to almost quantitatively extract the reaction products from the reaction mixture (which was confirmed by GLC). The quantitative extraction of menadione was performed by chromatography through silica gel (chloroform as an eluent), the solvent was distilled off, the amount of MD (in grams) was determined, and the yield was calculated. Then the ^{1}H NMR spectrum was recorded in CCl_4 (Fig. 1).

The purity of the isolated product was at least 98%. Silufol UV-254 plates were also used for express determination of MD. The IR spectra of the product were recorded on an IR-Affinity-1 spectrometer (Shimadzu, Japan) in KBr pellets.

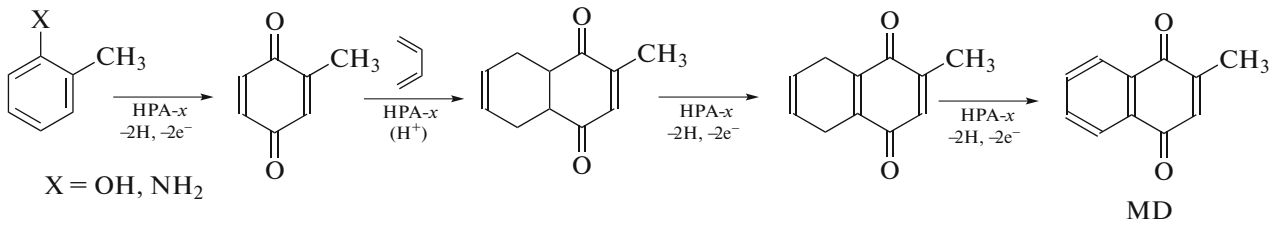
When *o*-toluidine was used as a substrate, the reaction mixture was filtered at the end of the reaction (before the extraction of the products) to separate the finely dispersed black precipitate, which was the product of the oxidative polymerization of *o*-toluidine.

The by-products of the conversion of 1,3-butadiene in the HPA-x solution were identified by chromato-mass spectrometry. The spectra were recorded on a GCMS-QP2010 Ultra spectrometer (Shimadzu, Japan).

The Mo–V–P-HPA-x ($x \geq 4$) solutions of various (Keggin and modified) compositions were prepared by the procedure described in [25, 26], and the solutions were regenerated in an autoclave at 160–180°C under oxygen pressure (P_{O_2} = 4 atm) by the procedure of [27]. The regenerated HPA-x solutions completely recovered their initial activity (initial E value); therefore, they were repeatedly used (for up to 30 cycles) in the target reaction (II). During the multicycle experiments, no vanadium-containing substance precipitated from solution. Low-vanadium HPA-x ($x \leq 3$) solutions were not used as the rate of their regeneration was significantly lower than that of the HPA-4 solution.

RESULTS AND DISCUSSION

Here, we solved the problem of synthesizing MD by diene synthesis from accessible substrates such as *o*-cresol (2-methylphenol) and *o*-toluidine (2-methylaniline) (Scheme 1). At the first stage of the study, the Keggin solution of HPA-4 ($H_7PMo_8V4O_{40}$) [28] was used as a bifunctional catalyst for this process.



Scheme 1. One-pot synthesis of menadione from *o*-cresol and *o*-toluidine in Mo–V–P-HPA-x solutions in a 1,3-butadiene atmosphere.

Table 1. Preparation of vitamin K_3 from *o*-cresol and *o*-toluidine by diene synthesis in the 0.2 M HPA-4 solution

Substrate, g/mmol	HPA-4, mL	HPA-4 : substrate molar ratio	*T*, °C	Yield of MD, %
o-Cresol, 0.27/2.5	18.8	1.5	80	18.9
	18.8	1.5	60	20.9
	18.8	1.5	40	16.7
	25.1	2.0	40	18.0
o-Toluidine, 0.13/1.25	6.5	1.0	80	20.0
	12.5	2.0	80	27.1
	12.5	2.0	60	28.5
	12.5	2.0	40	24.3
	23.5	3.75	40	21.1

Reaction conditions: 1,3-butadiene atmosphere, 2 h, 100% conversion of the substrate.

When these substrates are introduced in the HPA-4 solution in a 1,3-butadiene atmosphere (Scheme 1), they are first quickly oxidized to toluquinone, which is then condensed with 1,3-butadiene by the Diels–Alder reaction. At the final stages of the process, HPA-4 oxidizes the adducts of diene synthesis and is itself gradually reduced. The depth and rate of the process according to Scheme 1 are determined by the oxidizing capacity of the HPA-*x* solution, which can be expressed by the product [HPA-*x*] × Δm, where Δm is the change in the degree of reduction of HPA-*x* during the one-pot process [20]. We believed that the high concentration of V^V in the HPA-*x* solution would allow complete oxidation of the adducts of diene synthesis and a shift of the process according to Scheme 1 toward menadione.

A distinction of the new processes is that they are performed in one technological stage (i.e., are one-pot processes), and the ability of HPA-*x* solutions to be regenerated with oxygen by reaction (III) ensures the environmental friendliness of the method for the production of vitamin K_3. In addition, thorough washing of the organic phase and reaction products with water from possible impurities ensures the absence of traces of heavy metals (Mo, V) in the resulting vitamin K_3. Figure 1 shows the ^{1}H NMR spectrum of the isolated menadione.

Before studying the one-pot processes described by Scheme 1, the oxidations of *o*-cresol and *o*-toluidine to 2-methyl-1,4-benzoquinone (MBQ) were studied separately, and it was shown that these substrates were oxidized to MBQ with low yields (20–30%). It was assumed that in the presence of 1,3-butadiene, the rates of side processes, in particular, tar formation, could be reduced due to the fact that the Diels–Alder acid-catalyzed reaction would proceed simultaneously with the oxidation of *o*-cresol and *o*-toluidine in the HPA-*x* solution. In this case, the instant concentrations of the highly reactive radical particles in solution will be lower, due to which higher yields of MBQ and, accordingly, vitamin K_3 can be obtained in a one-pot process.

Table 1 presents the results of the study of the total synthesis of vitamin K_3 in accordance with Scheme 1. According to these data, the yield of MD does not exceed 21% when it is synthesized from *o*-cresol in the 0.2 M solution of HPA-4 in the presence of 1,3-butadiene and 29% in the synthesis from *o*-toluidine. In the case of *o*-cresol, which has high reactivity, tar forms in large amounts.

Both methods for the synthesis of vitamin K_3 certainly have disadvantages. Nevertheless, the synthesis from *o*-toluidine by diene synthesis looks slightly more promising than the synthesis from *o*-cresol. We expected that optimization of this process would make it possible to reduce polymer formation and thereby to increase the yield of MD.

In the case of *o*-toluidine, the low yield of MD was determined by the formation of a black precipitate of polytoluidine due to the oxidative polymerization of *o*-toluidine in HPA-4 solution at the first stage of the process simultaneously with the formation of the desired product according to Scheme 1. The IR spectrum of the obtained polymer is shown in Fig. 2.

The bands in the range 3200–3500 cm^{-1} are probably related to the vibrations of the N–H bond; the bands at 1600–1650 cm^{-1} are due to the C=N bond vibrations. The precipitate partially dissolved during the process and was oxidized to toluquinone. However, the bulk of it remained unchanged; thus, some part of the substrate was actually pulled out of the target process, which reduced the yield of MD.

The conditions of the one-pot synthesis of MD from *o*-toluidine were varied in order to reduce the contribution of the side reactions of substrate polymerization and an increase in the formation rate of vitamin K_3. In particular, *o*-toluidine was introduced in the reaction mixture in one portion and also by gradually dropping its dimethyl sulfoxide (DMSO) solution to reduce the instant concentration of the substrate in the HPA-4 solution. DMSO was chosen because of the partial solubility of polytoluidine in it; this was expected to facilitate further oxidation of the polymer to toluquinone. It turned out, however, that the intro-

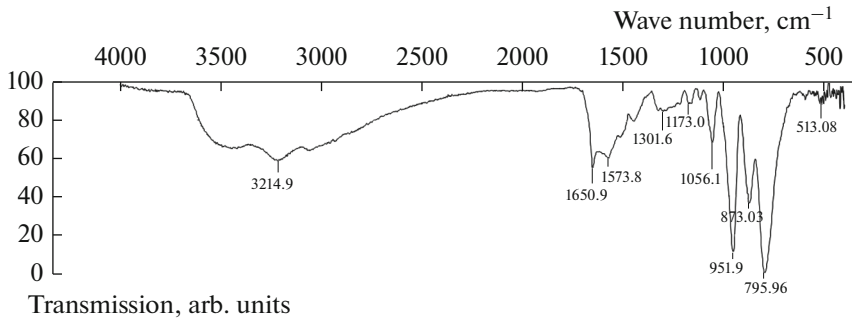


Fig. 2. IR spectrum of polytoluidine that precipitated from the HPA-4 solution during the preparation of vitamin K_3 from *o*-toluidine by diene synthesis in the presence of 1,3-butadiene.

duction of *o*-toluidine in the reaction mixture had almost no effect on the amount of the polymer product and, accordingly, on the final yield of MD.

For the same purpose, the one-pot process according to Scheme 1 was studied in the presence of an additional organic solvent (DMSO) in the reaction mixture. In this case again, however, the desired characteristics of MD synthesis from *o*-toluidine could not be improved. This suggests that polymerization of the substrate proceeds much more readily than its oxidation to toluquinone. Nevertheless, it is important that polytoluidine, which forms as a by-product in the oxidation of *o*-toluidine, does not completely drop out of the reaction. It can be separated from the reaction mixture, oxidized to 2-methyl-1,4-benzoquinone, and again introduced in the reaction according to Scheme 1. It also important that polytoluidine, like polyaniline, is a very valuable product: it has high electric conductivity and can be used as a current conductor in electric engineering [29].

For the one-pot processes using *o*-cresol and *o*-toluidine as substrates, the temperature was varied from 40 to 80°C. According to Table 1, the optimum temperature is 60°C in both cases.

To obtain a complete picture of possible products during the diene synthesis, we studied the possibility of side reactions of 1,3-butadiene in HPA-*x* solutions. For this purpose, blank experiments were performed, in which 1,3-butadiene was fed, in the absence of other substrates, into the HPA-*x* solutions (HPA-3, GPA-4, and GPA-6) for 5 h. An analysis of the reaction products showed that hydration of 1,3-butadiene into 3-buten-2-ol occurred at low rates, and the latter was further converted into methyl vinyl ketone (Scheme 2).

$$CH_2{=}CH{-}CH{=}CH_2$$
$$\rightarrow CH_2{=}CH{-}CH(OH){-}CH_3 \rightarrow CH_2{=}CH{-}COCH_3$$

Scheme 2. Transformation of 1,3-butadiene in aqueous solutions of Mo–V–P-HPA-*x*.

In addition, linear and branched oxygen-containing products of polymerization of 1,3-butadiene (molecular mass 122, 164, 166) were found in insignificant amounts. The total amount of by-products formed from 1,3-butadiene in the one-pot process in HPA-*x* solutions according to Scheme 1 did not exceed 2%.

In the case of *o*-cresol used as a substrate in the process according to Scheme 1, the main contribution to the formation of by-products is made by the oxidative polymerization of 2-methylphenol. Similar reactions of the oxidative polymerization of 2-methylnaphthol-1 were studied in [30], where it was shown that the selectivity of the catalyst based on the HPA-*x* solution with respect to menadione depends on the ratio of the rates of oxidative polymerization of intermediates and the formation of the desired product. The ratio, in turn, depends on the composition of HPA-*x* and the reaction method and conditions. In the developed Vikasib technology [30], a significant increase (from 45 to 90%) in the yield of menadione during the oxidation of 2-methylnaphthol-1 was achieved. We believed that the synthesis of vitamin K_3 from *o*-cresol according to Scheme 1 could also be optimized.

To solve this problem, modified HPA-*x* solutions of non-Keggin compositions with higher vanadium contents ($x = 7, 10$) were chosen at the second stage of the study of the possibility of using accessible raw materials for producing vitamin K_3 in HPA-*x* solutions by diene synthesis [25]. High vanadium concentrations in the modified solutions guarantee their increased oxidative capacity and hence productivity. For example, the V^V concentration in the 0.30 M modified solution of HPA-7 ($H_{10}P_3Mo_{18}V_7O_{84}$) is 2.6 times higher than in the 0.2 M solution of HPA-4 ($H_7PMo_8V_4O_{40}$) often used in catalytic reactions. Due to this V^V concentration, the modified HPA-*x* solutions retain their high oxidative potential E [20] throughout the whole process according to Scheme 1, guaranteeing complete oxidation of the adducts of diene synthesis to vitamin K_3.

Another important fact is high stability of the modified HPA-*x* solutions; they remain homogeneous up to 180°C (the maximum temperature for fast regener-

Table 2. Preparation of vitamin K_3 from *o*-toluidine by diene synthesis in the 0.25 M solutions of HPA-7, HPA-10, and HPA-4

o-Toluidine, g/mmol	HPA-*x*, mL	HPA-*x* : *o*-toluidine molar ratio	*T*, °C	Yield of MD, %
0.107/1.0	HPA-7; 20	5	40	27.2
0.107/1.0	HPA-7; 12	3	40	28.1
0.107/1.0	HPA-7; 12	3	60	32.4
0.107/1.0	HPA-7; 12	3	80	30.0
0.064/0.6	HPA-7; 12	5	60	31.2
0.107/1.0	HPA-10; 20	5	40	28.0
0.107/1.0	HPA-10; 12	3	40	28.5
0.107/1.0	HPA-10; 12	3	60	32.8
0.107/1.0	HPA-10; 12	3	80	29.9
0.107/1.0	HPA-10; 8	2	60	32.3
0.064/0.6	HPA-10; 12	5	60	32.6
0.107/1.0	HPA-4; 20	5	60	27.3
0.107/1.0	HPA-4; 8	2	60	28.0

Reaction conditions: 1,3-butadiene atmosphere, 2 h, 100% conversion of the substrate.

ation of HPA-*x* solutions), providing long life of catalysts based on them [20]. Based on all these factors, we believed that the catalysts based on modified HPA-*x* could be promising for use in one-pot processes according to Scheme 1.

Note that when MD was obtained from *o*-cresol in the presence of both HPA-7 and HPA-10, it was impossible to obtain a higher yield of the desired product than with HPA-4 (21%). With this substrate, the side processes of tar formation in HPA-*x* solutions occur much more easily than diene synthesis, although the acidity of the modified HPA-*x* solutions is significantly higher than that of the HPA-4 solution [20]. It was assumed that by increasing the acidity of the catalyst solution it would be possible to increase the rate of the reaction of *o*-cresol and 1,3-butadiene (acid-catalyzed reaction), but this did not happen. Therefore, there is some other reason for the low yield of MD. The acidity of the HPA-4 solution was already high enough for effective diene synthesis; nevertheless, the rate of the side reactions of *o*-cresol condensation was high in all HPA-*x* (Keggin and modified) solutions. Therefore, our study focused on the synthesis of MD from *o*-toluidine.

Table 2 presents the data obtained by studying the one-pot synthesis of vitamin K_3 in accordance with Scheme 1 from *o*-toluidine in the presence of 1,3-butadiene in solutions of modified high-vanadium HPA-7 ($H_{10}P_3Mo_{18}V_7O_{84}$) and HPA-10 ($H_{17}P_3Mo_{16}V_{10}O_{89}$). For comparison, the table gives the data for HPA-4.

Analyzing the results, we can conclude that the optimum temperature of the one-pot synthesis of MD from *o*-toluidine in modified high-vanadium HPA-*x* solutions is 60°C, as in the presence of Keggin HPA-4.

It can be seen that excess V^V concentration is not required for complete oxidation of the adducts of diene synthesis in accordance with Scheme 1, as in the HPA-7 and HPA-10 solutions. For these HPAs-*x*, the highest yields of MD (~32%) are observed at a molar ratio of HPA-*x* to *o*-toluidine of 2–3. The oxidative potential of these solutions remains high enough throughout the one-pot process (above 0.85 V relative to SHE), providing complete oxidation of the adducts. Clearly, due to the side reactions at the first stage of the process, the amount of these adducts is only ~30% of the theoretical value.

Another possibility of increasing the MD yield in the overall process according to Scheme 1 was studied. For this purpose, an organic solvent dioxane was added to the reaction mixture before the experiment, which is effective in two-phase organic reactions [31]. It was assumed that a water-miscible solvent would facilitate the mixing of the two phases, reduce the substrate concentration in the organic phase, and thus would reduce the side processes of condensation. It was found, however, that the presence of dioxane did not affect the final yield of MD in any way.

Thus, it was shown that vitamin K_3 can be obtained from *o*-toluidine in solutions of modified Mo–V–P-HPAs-*x* with a yield of up to 33% according to Scheme 1. The polytoluidine by-product obtained in this process may be used, for example, in electrotechnical industry [29].

CONCLUSIONS

The possibility of the catalytic production of vitamin K_3 in the presence of HPA-*x* solutions in one technological stage from *o*-cresol and *o*-toluidine in a 1,3-butadiene atmosphere was shown. In this case, HPA-*x* acts as a bifunctional (acid and oxidative) catalyst. Despite the low yield of the desired product (below 33%), the new method is attractive because menadione is synthesized from accessible raw materials and the multistage process is performed in one technological stage. The regeneration of HPA-*x* solutions with oxygen opens up prospects for the development of new methods for the synthesis of vitamin K_3 in the presence of HPA-*x* as a bifunctional catalyst.

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