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Low-Waste One-Pot Process for Obtaining Anthraquinone through Diene Synthesis in the Presence of the Solutions of Heteropolyacids

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Abstract

Acid catalytic condensation of 1,3-butadiene with *para*-quinones and the oxidation of resulting adducts can be performed in one technological stage in the presence of the aqueous solutions of Mo–V–P heteropolyacids (HPA) of general composition $H_a P_z Mo_y V_x O_b$. These solutions possess bifunctional catalytic properties being strong Brønsted acids and rather strong reversibly acting oxidizers at the same time. The condensation of 1,4-naphthoquinone with 1,3-butadiene in HPA solutions leads to obtaining 9,10-anthraquinone (AQ) in mixture with tetrahydroanthraquinone (THA) and dihydroanthraquinone (DHA). In the course of a single-stage process without organic solvents, the HPA solution is reduced and poorly soluble mixture of THA, DHA and AQ (up to 50 %) precipitates almost quantitatively from the solution. The yield and purity of AQ can be improved substantially due to the use of organic solvents miscible with water (for example, acetone, 1,4-dioxane), as well as high-vanadium HPA of the composition $H_{15}P_4Mo_{18}V_7O_{89}$ and $H_{17}P_3Mo_{16}V_{10}O_{89}$. Optimization of the process allowed us to obtain the product containing not less than 90 % AQ. Results achieved in the work open outlooks for the development of low-waste process for the production of AQ from 1,3-butadiene and 1,4-naphthoquinone.

Key words: anthraquinone, heteropolyacids, diene synthesis

INTRODUCTION

9,10-Anthraquinone (AQ) is important product of organic synthesis [1]. One of the industrial methods to synthesize 1,4,4a,9a-tetrahydroanthraquinone-9,10 (THA), 1,4-dihydroanthraquinone-9,10 (DHA) and AQ is diene synthesis, which is based on the catalytic gas-phase oxidation of naphthalene into 1,4-naphthoquinone (NQ) and the reaction of the latter with 1,3-butadiene [1]. The primary products of addition (adducts) are obtained in organic solvents under the pressure of butadiene 0.3–2 MPa or in the presence of organic acids (to reduce pressure). The adduct of diene synthesis (THA) isomerises under the action of acids or alkalis into 1,4-dihydro-9,10-dihydroxyanthracene, and the latter is further oxidized (to form DHA and AQ) by strong oxidizers in acid medium (CuCl₂, H₂O₂ or NaClO₃ [2]) or by atmospheric oxygen in the alkaline medium [3].

Oxidation of various organic substrates by oxygen can be carried out in the presence of the aqueous solutions of Mo–V–P heteropolyacids (HPA). This process usually takes place in two stages. At the first stage the substrate (Su) is oxidized by the HPA solution according to reaction

$$(m/2)Su + (m/2)H_2O + HPA \rightarrow (m/2)SuO + H_mHPA \quad (1)$$

At the second stage the reduced form of HPA (H_mHPA) is oxidized by atmospheric oxygen [4–6]:

$$H_mHPA + (m/4)O_2 \rightarrow HPA + (m/4)H_2O \quad (2)$$

So, HPA solutions act in catalytic processes (1) and (2) as reversible oxidizers in which redox transformations are underwent by vanadium atoms ($V^V \rightarrow V^{IV} \rightarrow V^V$).
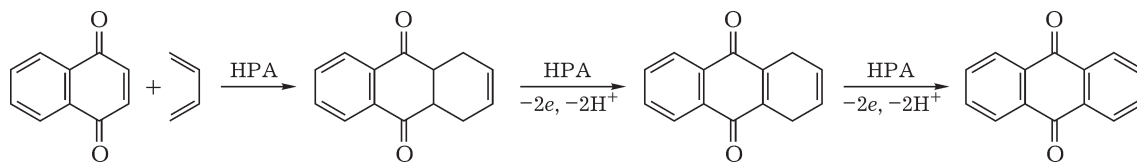
Scheme 1. One-pot process of AQ formation through the diene synthesis in the solutions of Mo−V−P HPA.

Previously [7, 8] we proposed to use the aqueous solutions of Mo−V−P HPA, which are at the same time acid catalysts and rather string oxidizers, for obtaining AQ through the reaction of 1,4-naphthoquinone with 1,3-butadiene. The use of HPA solutions as bifunctional catalysts allows one to carry out the synthesis of AQ in one technological stage, that is, for perform a one-pot process (Scheme 1). After the process, reduced HPA solution may be separated from the solid precipitated product by filtering and regenerated, for example by oxygen at increased pressure [9]. In this case, the overall process of AQ synthesis in the presence of HPA solution may be considered as catalytic: diene synthesis is catalysed by HPA, while the oxidation of the formed adduct into AQ by atmospheric oxygen is catalysed by vanadium-containing HPA.

In [7, 8], in the interaction of butadiene with NQ in the presence of HPA solution we obtained the mixtures of products containing in addition to AQ also partially hydrated products (THA and DHA). In the present work we carried out optimisation of the conditions of one-pot process for the purpose of obtaining practically pure product. The conditions under which the stages of the oxidation of adducts of diene synthesis are almost completely shifted to the target product have been determined.

EXPERIMENTAL

We used 1,4-naphthoquinone and 9,10-anthraquinone from Alfa Aesar Co. In all experiments, 1,3-butadiene (C_4H_6) of 99 % purity was used. Tetrahydroanthraquinone and DHA were synthesized using the known procedures [10].

In experiments, we used the solutions of 0.2 M HPA-x (x is the number of vanadium atoms in HPA) of different overall compositions: HPA-4 of Keggin composition ($H_7PMo_8V_4O_{40}$), high-vanadium non-Keggian solutions of HPA-7 ($H_{15}P_4Mo_{18}V_7O_{89}$) and HPA-10 ($H_{17}P_3Mo_{16}V_{10}O_{89}$). The HPA solutions were synthesized according to the procedure described in [11].

Analysis of reaction products was carried out by means of HPLC. For this purpose, liquid chromatograph ProStar was used. It was equipped with a ProStar 410 AutoSampler, ProStar210, ProStar218 Solvent Delivery Module, Varian 500-LC Column Volve Module and UV detector Photodiode ProStar 335 (wavelength 247 nm). Product separation was carried out with a Pursuit 3 C18 column (247×4.6 mm) at the eluent flow rate of 1 mL/min. The solvents used for chromatographic examination were manufactured by companies: methanol − J. T. Baker, 99.9 %, UV-IR-HPLC; acetonitrile − Panreac, 99.9 %, HPLC gradient grade, PАl-ACS; trifluoroacetic acid − Acron Organics, 99 %, os. ch. grade and deionised water (deionised using a Barnstead EASYpure RF Seris 1051). Eluent composition was: 70 % CH_3OH + 30 % CF_3COOH (solvent for samples was chloroform).

The synthesis of AQ was carried out in a thermostated autoclave made of stainless steel with a glass beaker inserted, into which 15.6 mL of the solution of 0.2 M HPA and 0.2 g of the substrate (NQ) were added. In the case when organic solvent was used, the substrate was preliminarily dissolved in it. Then the autoclave was connected to a pressure vessel with butadiene and blown through to remove air at a given temperature and without mixing. After that, the jacket of the autoclave was connected to the thermostat heated preliminarily to the required temperature, and mixing started. All the syntheses of AQ were carried out under intense mixing of the reaction mixture with a magnetic stirrer (650 min^{-1}) for 1−9 h in the atmosphere of butadiene. The HPA solution was reduced during the synthesis [12] changing its colour from dark-red to green or dark-blue.

Poorly soluble solid products were precipitated from the reduced HPA solutions: AQ and its partially hydrogenated derivatives (in the absence of organic solvents − usually up to 97 % of the obtained amount). They were separated by filtering, washed with water and dried above P_2O_5 in vacuum. The residues of products (in the presence of organic solvents − up to 10 % of the obtained amount) were extracted from the reduced HPA solution by chloroform (3×30 mL). The extract was dried above $MgSO_4$ and evaporated till the formation of dry substance. The united dry residue was weighted and then analyzed by means of HPLC.

The degree of NQ conversion (X_{NQ}) was calculated according to equation

$$X_{NQ} = (MC_{NQ} \cdot 100)/M_{NQ}$$

where M is the mass of the dry precipitate of the products, g; C_{NQ} is the fraction of NQ in the precipitate according to analysis data; M_{NQ} is the weighted portion of initial NQ, g.

Reduced HPA solution was regenerated in a thermostated autoclave similar to the above-described one with a glass beaker inserted at $P_{O_2} = 200−400$ kPa under mixing at $140−160$ °C for $25−30$ min [9].

RESULTS AND DISCUSSION

To determine the optimal reaction time, the dependence of NQ conversion degree on reaction duration was obtained. Below we present the data on the degree of naphthoquinone conversion (X_{NQ}) on reaction time (τ) under the following process conditions: 15.6 mL of the aqueous solution of 0.2 HPA-4, molar ratio HPA-4/NQ = 2, butadiene pressure $P = 150$ kPa, temperature 80 °C:

τ, min	60	80	120	300	540
X_{NQ}, %	58.7	66.8	99.2	98.2	98.1

One can see that almost complete transformation of NQ is achieved within 2 h. At the same time, it is known [10] that heating for 3 h at 100 °C is required for the reaction of butadiene with NQ to be completed without a catalyst in ethanol. So, the use of HPA solution catalyses diene synthesis accelerating it notably.

As we have already mentioned above, in [7, 8] when performing a one-pot process of NQ synthesis under atmospheric pressure and $T = 80−$ 90 °C in the absence of organic solvent or in the presence of an immiscible solvent (chloroform, trichloroethylene), we obtained mixtures of four compounds (traces of NQ + THA + DHA + AQ, see Scheme 1) containing not more than 50 % AQ. In this connection, it may be assumed that the rate of the oxidation of adducts formed in diene synthesis into AQ may be increased by rising process temperature. However, temperature rise to 135 °C required substantial butadiene pressure (to compensate for the high partial pressure of water) and did not cause a substantial increase in AQ content. Moreover, the major reaction product (up to 65 % of the total mass of precipitate) at temperatures above 100 °C turned out to be THA. This is likely to be due to lower (than in the case of the temperature of 90 °C) butadiene pressure, which limits the process of diene synthesis and therefore the whole process of AQ synthesis. Subsequent studies were carried out at temperatures below 100 °C.

In addition, we assumed that incomplete oxidation of the adduct of diene synthesis in the presence of aqueous solutions of HPA is due to the heterogeneous composition of the reaction mixture. 1,4-Naphthoquinone is poorly soluble in HPA solution; THA and DHA are poorly soluble even under heating; nonpolar organic solvents that were used in previous experiments were immiscible with HPA solution. In this connection, the oxidation of adducts at the interface proceeds rather slowly. One of the versions to optimise the conditions of one-pot synthesis of pure AQ may be the use of organic solvents that can dissolve HPA and are mixable with water. A compulsory additional requirement is the stability of such a solvent against the action of HPA (rather strong oxidizers).

Results of experiments with several hydrophilic solvents are shown in Table 1. One can see that the use of acetone and 1,4-dioxane allows obtaining a product containing mainly AQ and DHA. The concentration of THA and initial NQ in the product is very low. With dimethylsulphoxide (DMSO) and especially isopropanol, the results on NQ conversion were substantially worse. The observed changes in the concentrations of reaction products are likely due to incomplete solubility of the substrate in the organic solvent.

TABLE 1

Dependence of the parameters of one-pot AQ synthesis on solvent nature. Conditions: 15.6 mL of the aqueous solution of 0.2 M HPA-4, the molar ratio of HPA-4 to NQ is 2, butadiene pressure $P = 200$ kPa $- P_{H_2O}$, reaction time 7 h, volume of organic solvent 8 mL

Solvents	T, °C	Reaction products, mol. %				X_{NQ}, %	Yield of AQ, %
		AQ	THA	DHA	NQ		
Water*	80	51.7	22.9	16.0	4.1	97.1	27.9
Acetone	60	83.4	1.8	12.6	0.4	99.5	73.4
Isopropanol	80	58.0	16.5	17.0	3.4	97.3	35.7
DMSO	80	72.3	9.9	13.3	0.8	99.7	22.8
1,4-Dioxane	80	84.5	–	14.7	0.2	99.8	69.7

Notes. 1. Here and in Tables 2, 3: % the yield of AQ was calculated as the ratio of the mass of the obtained AQ to its theoretically possible amount. 2. Water pressure at 60 °C is equal to 20 kPa, at 80 °C it is 47 kPa, at 90 °C it is 70 kPa.

* Reaction time is 9 h.

In the case of acetone, we determined the optimal volume ratio acetone/HPA solution (Table 2). It turned out that with an increase in this ratio the yield of AQ increases substantially. This is connected with an increase in the amount of dissolved NQ; we determined that it is completely dissolved in the reaction mixture with the volume ratio of acetone to HPA solution equal to 0.5. Under these conditions, the yield of AQ (73.4 %) turned out to be higher than in the absence of organic solvent, with other conditions kept identical (27.9 %, see Table 1). Reaction product contains AQ 83 %, DHA 12 %, the rest is a mixture of NQ and THA. Further increase in the indicated ratio is unreasonable because the amount of dissolved AQ increases, and it is necessary to extract it from the reaction mixture after the process.

In the presence of the indicated solvents, the mixture still contains some amount of DHA,

TABLE 2

Dependence of the parameters of one-pot process of AQ synthesis on the volume ratio acetone/HPA-4 solution. Conditions: 15.6 mL of the aqueous solution of 0.2 M HPA-4, molar ratio HPA/NQ = 2, butadiene pressure $P = 200$ kPa $- P_{H_2O}$, temperature 60 °C, reaction time 7 h

Parameters	Volume ratio acetone/HPA-4 solution		
	0.32	0.42	0.51
X_{NQ}, %	99.3	99.4	99.5
AQ yield, %	17.9	41.9	73.4

Note. For designations, see Table 1.

so instead of Keggin HPA-4 solution we also tested HPA-x solutions with higher vanadium content (HPA-7 and HPA-10) conserving the high oxidation potential during the whole process [13] (Table 3).

One can see that using HPA-7 and acetone as organic solvent in one-pot process, a mixture of products containing 91.6 % AQ and 8.3 % DHA was obtained. The use of HPA-10 solution and dioxane as solvents at a temperature of 90 °C and reaction time 7 h allowed us to obtain the product with AQ content 97 % (the rest is DHA). The degree of NQ conversion was 99.7 %, and the yield of AQ was 67 %.

So, the joint use of organic solvent mixable with water and HPA-10 solution which is a stronger oxidizer than Keggin HPA-4 solution allows obtaining practically pure AQ; the major part of this product (about 90 %) is separated from the reduced solution by simple filtering. The rest 10 % of the product may be extracted from the solution by chloroform.

Before regeneration of the catalyst according to reaction (2) by oxygen [9], the solvents are distilled from the reaction mixture: acetone in the pure form, 1.4-dioxane in the form of aqueous azeotrope (m. p. 88 °C) containing dioxane 82 %. Regenerated solvents are used many times at the subsequent cycles of the process of AQ synthesis.

High-vanadium solutions of HPA-7 and HPA-10 possess rather high thermal stability. They conserve their homogeneity at temperatures up to 170 °C and allow rapid regenera-

TABLE 3

Dependence of the parameters of one-pot process of AQ synthesis on the composition of HPA-x. Conditions: 15.6 mL of the aqueous solution of 0.2 M HPA-x, molar ratio HPA-x/NQ = 2, butadiene pressure P = 200 kPa $-$ $P_{\text{H}_2\text{O}}$, the volume of organic solvent 8 mL

HPA-x	Solvent	Reaction time, h	T, °C	AQ content in the product, %	X_{NQ}, %	AQ yield, %
HPA-4	Water	5	80	46.5*	97.2	17.7
HPA-7	«	5	80	74.6*	99.5	17.9
HPA-10	«	5	80	75.5*	98.9	23.0
HPA-7	Acetone	7	60	91.6**	99.6	65.0
HPA-4	1,4-Dioxane	7	80	84.5*	99.8	69.7
HPA-10	1,4-Dioxane	7	90	96.9**	99.7	67.0

* The product also contains THA and DHA.

** The product also contains DHA.

tion of the catalyst by oxygen at increased temperatures [9]. High-vanadium solutions of HPA are efficient catalysts of oxidation, with the working oxidation potential within the range 1.1−0.75 V. The presence of these compounds will allow one to carry out the one-pot process of AQ synthesis many times.

CONCLUSION

Optimization of the conditions was carried out for a single-stage process of 9,10-anthraquinone synthesis according to the reaction of 1,4-naphthoquinone with 1,3-butadiene in the presence of Mo−V−P HPA solutions as bifunctional catalysts: acid catalysts of diene synthesis and catalysts of the oxidation of adducts formed.

It is demonstrated that to obtain the high AQ content in the product (above 90 %) and its high yield (about 70 %) it is necessary to use polar water-mixable organic solvent (for example, acetone, 1,4-dioxane). The solvent can be regenerated and used repeatedly at the subsequent cycles of the process. The best parameters of a one-pot AQ synthesis process are provided by the use of Mo−V−P HPA-10 of overall composition $H_{17}P_3Mo_{16}V_{10}O_{89}$ as a bifunctional catalyst.

The results obtained in the work open the outlooks for the creation of low-waste single-stage process for the production of AQ from 1,4-butadiene and NQ.

REFERENCES

1 Gorelik M. V., Khimiya Antrakhinonov i Ikh Proizvodnykh, Khimiya, Moscow, 1983.
2 KR Pat. No. 2001004856, 2001.
3 KR Pat. No. 2000001821, 2000.
4 Kozhevnikov I. V., *Chem. Rev.*, 98 (1998) 171.
5 Zhizhina E. G., Simonova M. V., Odyakov V. F., Matveev K. I., *Appl. Catal. A: Gen.* 319 (2007) 91.
6 Zhizhina E. G., Simonova M. V., Odyakov V. F., *Kinet. Katal.*, 49 (2008) 773.
7 Zhizhina E. G., Matveev K. I., Russkikh V. V., *Chem. Sustain. Dev.*, 12, 1 (2004) 47.
URL: http://www.sibran.ru/en/journals/KhUR
8 Zhizhina E. G., Odyakov V. F., *ChemCatChem*, 4 (2012) 1405.
9 Zhizhina E. G., Simonova M. V., Odyakov V. F., Matveev K. I., *Chem. Sustain. Dev.*, 12, 6 (2004) 683. URL: hhtp://www.sibran.ru/en/journals/KhUR
10 Hickinbottom W. J., Reactions of Organic Compounds, Longmans, New York, 1936.
11 Odyakov V. F., Zhizhina E. G., *Zh. Neorg. Khim.*, 54 (2009) 409.
12 Odyakov V. F., Zhizhina E. G., Matveev K. I., *Zh. Neorg. Khim.*, 45 (2000) 1258.
13 Odyakov V. F., Zhizhina E. G., *Appl. Catal. A: Gen.*, 358 (2009) 254.