ONE-POT PROCESSES OF PARA-QUINONES SYNTHESIS IN THE PRESENCE OF MO–V–P HETEROPOLY ACIDS SOLUTIONS

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1. Introduction .

Quinones are a class of organic compounds with a number of important properties. Therefore, at present new methods for the quinone synthesis are of great demand. One of methods of quinones production is diene synthesis from benzoquinone (BQ) or 1,4-naphthoquinone (NQ) and 1,3-dienes in the presence of oxidizers [1-2].

As oxidizers Mo-V-P heteropoly acids $H_{3+x}PV^V_xMo_{12-x}O_{40}$ (HPA-x) can be used. Unlike many other oxidizing agents, the vanadium-containing HPA solutions are able to be regenerated by O_2. Thus they can catalyze the two-stages oxidation of various substrates by O_2. It is known also that vanadium-containing HPA-x solutions can be used as acid catalysts of cycloaddition reaction (diene synthesis) for getting *para*-quinones from quinones and 1,3-dienes [3]. Therefore, HPA-x solutions can be bifunctional (i.e. oxidative and acidic) catalysts in this *one-pot* process.

2.RESULTS AND DISCUSSION.

We have developed new processes of quinones production from hydroquinone (HQ) or NQ in the presence of HPA-x solutions [3-5]. At that, we have combined *in a single technological stage* three types of reactions: 1) oxidation of HQ by HPA-x to BQ; 2) the acidic-catalyzed Diels-Alder reaction of different 1,3-dienes (1 or 2 mol) with BQ or NQ giving substituted 1a,4a-tetrahydro-NQ (THNQ) or 1,4,4a,9a-tetrahydroanthraquinone (THAQ) respectively; 3) the sequential oxidation of THNQ or THAQ by HPA-x with the formation substituted NQ or AQ. Thus, our *one-pot* processes are described by the following scheme :
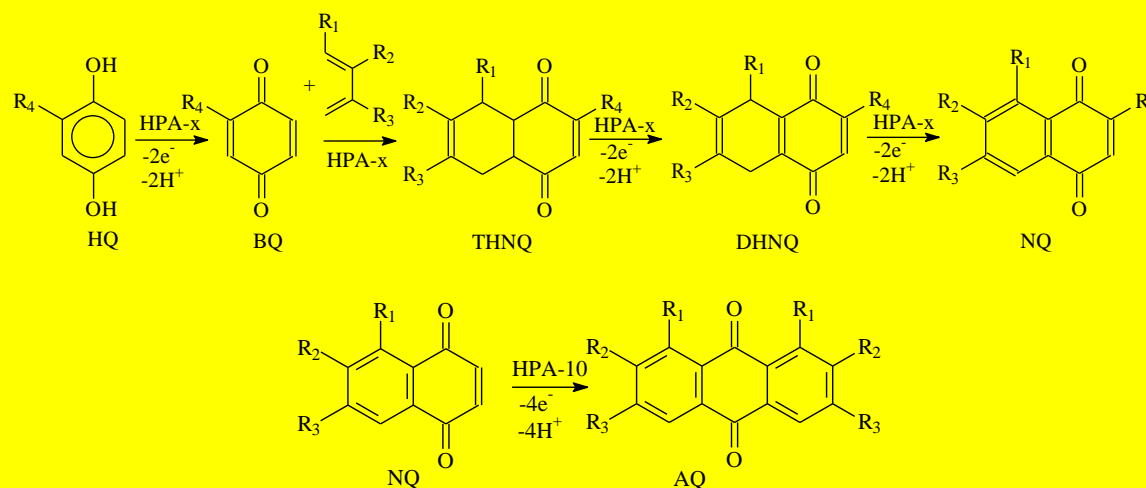
Results are presented in the Table.

In the industrial version, these processes can be realized in separate reactors **1** and **2**. In the 1st stage a substrate is oxidizing by HPA-x. In the 2nd stage HPA-x is regenerated by O_2.

Table.

№	Substituents	Yield of product, %	Content main product in precipitate, %
	a) Naphthoqinones		
1	$R_1 = H$, $R_2 = CH_3$, $R_3 = R_4 = H$	63	98
2	$R_2 = R_3 = R_4 = H$, $R_1 = CH_3$	62	97
3	$R_2 = R_3 = CH_3$, $R_1 = R_4 = H$	72	90
4	$R_1 = R_2 = R_3 = R_4 = H$	51	99
5	$R_1 = R_2 = R_3 = H$, $R_4 = CH_3$	32	96
	b) Anthraquinones		
6	$R_1 = H$, $R_2 = R_3 = CH_3$	78	98
7	$R_1 = R_2 = R_3 = H$	70	97
8	$R_1 = R_3 = R_4 = H$, $R_2 = CH_3$	72	96
9	$R_1 = R_3 = R_4 = H$, $R_1 = CH_3$	91	99

Conditions: a) 2×10^{-3} mol HQ, 10 mL 0.25 M $H_7PMo_8V_4O_{40}$ (HPA-4) water solution, volume ratio HPA-4 : 1,4-dioxane = 1 : 1, reaction time 30 h, temperature 20 °C. HQ conversion ≥ 99%;
b) 1.3×10^{-3} mol NQ, 3,9 mL 0.20 M $H_{17}P_3Mo_{16}V_{10}O_{89}$ (HPA-10) water solution, volume ratio HPA-10 : 1,4-dioxane = 1 : 2; reaction time 7 h, temperature 80 °C. NQ conversion ≥ 99%.

At the 1st stage, solutions of catalyst and substrate react in a jacketed glass reactor equipped with agitator and reflux condenser in the absence of oxygen. After reaction completion, the obtained mixture is transferred to a filter where solid product are filtered away. After that catalyst solution is submitted to an unique plug-flow air reactor and regenerated for 20-25 min at 160-170°C and $PO_2 = 0.4$ MPa. The regenerated HPA-x catalyst is fed again for the next catalytic cycle.

3. REFERENCES
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4. ACKNOWLEDGEMENTS.