

Catalytic Synthesis of 1,4-Naphtho- and 9,10-Anthraquinones According to the Diene Synthesis Reaction for Pulp and Paper Industry

ELENA G. ZHIZHINA¹, KLAVDIY I. MATVEEV¹ and VLADIMLEN V. RUSSKIKH²

¹Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 5, Novosibirsk 630090 (Russia)

E-mail: zhizh@catalysis.nsk.su

²Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 9, Novosibirsk 630090 (Russia)

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Abstract

It was established that the adducts of the diene synthesis of 1,4-benzo- and 1,4-naphthoquinones with butadiene get oxidized by Mo–V-phosphorus heteropolyacids (HPA) and their salts in a two-phase system to form 1,4-naphtho- and 9,10-anthraquinones. The promising character of the multistage catalytic synthesis of 1,4-quinones in the presence of HPA within a single technological operation was demonstrated.

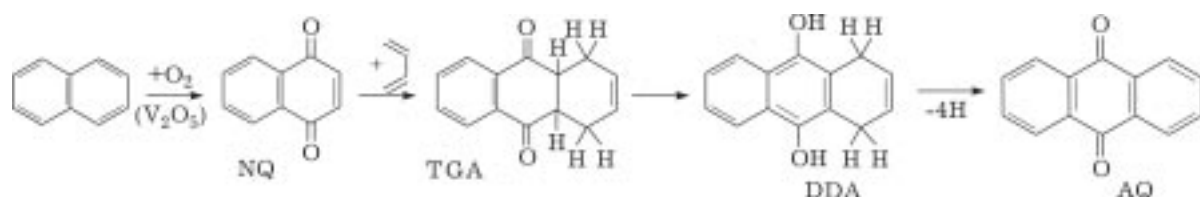
INTRODUCTION

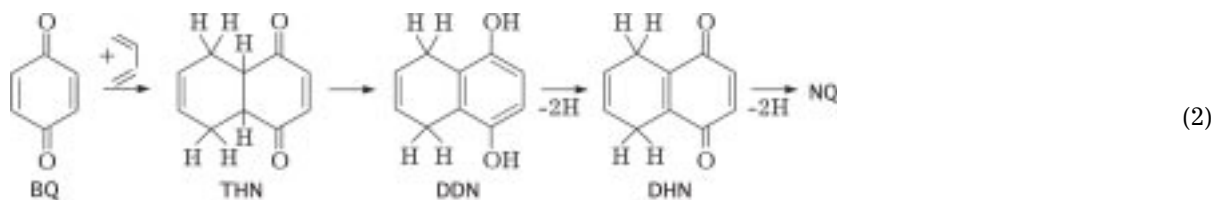
Wide application of ecologically safe methods of cellulose pulping in pulp and paper industry is due to the use of wood delignification catalysts. Among the compounds of different complexity exhibiting catalytic efficiency in pulping processes, wide application in the countries with the developed pulp and paper industry has been won by the adducts of the diene synthesis of 1,4-naphthoquinone with 1,3-butadiene, such as 1,4,4a,9a-tetrahydroanthraquinone (THA), 1,4-dihydro-9,10-dihydroxyanthracene (DDA) and 9,10-anthraquinone (AQ) [1].

The latter compound and its derivatives are also semiproducts for the synthesis of various highly stable dyes.

One of the industrial methods of production of THA, DDA and AQ is based on catalytic gas-phase oxidation of naphthalene into 1,4-naphthoquinone (NQ) and its subsequent reaction with 1,3-butadiene (Scheme (1)) [2]. A similar reaction of 1,4-benzoquinone (BQ) with 1,3-butadiene is the basis for the efficient preparative method of obtaining NQ (Scheme (2)) [3].

Undoubtedly, diene synthesis on the basis of quinones and other cyclenones provides broad possibilities for obtaining polycyclic aro-

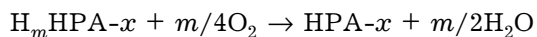




DDN is 1,4-dihydroxy-5,8-dihydronaphthalene, DHN is 5,8-dihydronaphthalenedione-1,4.

matic systems [4]. The primary products of the condensation of 1,3-butadiene with NQ and BQ (or adducts), that is, 1,4,4a,9a-tetrahydroanthraquinone-9,10 (THA) and 4a,5,8,8a-tetrahydronaphthaquinone (THN), which are obtained in organic solvents under increased pressure or in the presence of organic acids to reduce pressure, are partly hydrogenated quinones. They were transformed into quinones by non-catalytic dehydrogenation (oxidation). As regards oxidizers, the action of oxygen of the air in alkaline medium and a number of other stronger oxidizing agents under different conditions was investigated [5]. As a rule, all the existing methods are ecologically not sound, that is why search for more perfect methods of oxidative dehydrogenation of the adducts of diene synthesis of quinones goes on.

The goal of the present investigation is the development of catalytic processes of synthesis of 1,4-quinones in the presence of Mo-V-phosphorus heteropolyacids heteropoly acids (HPA-*x*, where *x* is the number of vanadium atoms). On the one hand, these compounds can exhibit catalytic activity as proton-bearing acids [6] at the stage of condensation of quinone with 1,3-butadiene to form an adduct, on the other hand, they can be dehydrogenating oxidizers of the adduct to form a quinone with an additional aromatic ring. The HPA-*x* compounds are oxidizing agents of reversible action, since their reduced forms ($H_m\text{HPA-}x$) get oxidized into HPA-*x* by molecular oxygen according to the reaction



Because of this, HPA-*x* are also catalysts of the stage of adduct oxidation into quinone by molecular oxygen.

EXPERIMENTAL

Aqueous solutions of Mo-V-phosphorus heteropolyacids heteropoly acids of Keggin struc-

ture of the composition $\text{H}_7\text{PMo}_8\text{V}_4\text{O}_{40}$ (HPA-4), $\text{H}_9\text{PMo}_6\text{V}_6\text{O}_{40}$ (HPA-6) of the required concentrations, and the acidic salt of HPA-6 of the composition $\text{NaH}_8\text{PMo}_6\text{V}_6\text{O}_{40}$ were obtained using the procedure described in [7].

Partially hydrogenated 1,4-quinones (THN, DDN, DHN, THA, DDA and DHA (1,4-dihydroanthraquinone-9,10)) were synthesized according to procedures described in [9, 10] [8, 9].

The ^1H NMR spectra were recorded with Bruker WP-200 SY spectrometer with CDCl_3 as a solvent. The concentrations of components in mixtures were determined using the ratios of integral intensities of proton signals for BQ at 6.72 ($\text{H}^2, \text{H}^3, \text{H}^5, \text{H}^6$), NQ – at 8.28 ($\text{H}^1, \text{H}^4, \text{H}^5, \text{H}^8$), DHN – at 3.01 ($2\text{H}^5, 2\text{H}^8$), DHA – at 3.20 ($2\text{H}^1, 2\text{H}^4$), THN – at 2.19–2.54 ($2\text{H}^5, 2\text{H}^8$), DDN – at 3.16 ($2\text{H}^5, 2\text{H}^8$), THA – at 2.18–2.55 ppm ($2\text{H}^1, 2\text{H}^4$).

Oxidative dehydrogenation was carried out in a thermostated 100 ml cone flask with a backflow condenser. Mixing was performed with a magnetic mixer. In the case of the reaction with the two-phase system (aqueous solution of HPA-*x* and the solution of the substrate in organic solvent), the products of reaction were separated from the catalyst by means of phase separation. When the reaction was performed without organic solvent, the solid reaction products were separated by filtering the HPA-*x* solution. To achieve more complete isolation of the reaction products, this solution was extracted with organic solvent (chloroform, benzene); the extract was dried with anhydrous CaCl_2 and evaporated till dry. The content of components in the resulting mixture of products was estimated with the help of ^1H NMR spectra. Their yield was determined by separating the mixture on chromatographic columns with silica gel (elutriators: *n*-hexane, benzene, chloroform). The results of experiments are shown in Table 1.

TABLE 1

Results of experiments on oxidative dehydrogenation of partially hydrogenated quinones in the presence of aqueous solution of 0.25 M $H_7PMo_8V_4O_{40}$ (HPA-4) (in each experiment, 22.5 ml of 0.25 M solution of HPA-4 (5.62 mol) was used)

Substrate (S)	Charging			Reaction conditions		Yield, %		
	S, mmol (g)	HPA : S molar ratio	Solvent, ml	T, °C	Time, h	Quinone	Dihydro- quinone	Initial substrate
DDN	1 (0.162)	5.62	Octanol, 10	65	2.5	NQ, 67		Absent
»	2 (0.342)	2.81	Octanol, 4	68	2.5	NQ, 62		»
»	4 (0.648)	1.40	»	68	1	NQ, 68		»
»	4 (0.648)	1.40	Chloroform, 5	50	1	NQ, 30	DHN, 59	3
»	4 (0.648)	1.40	Absent	70	1	NQ, 82	DHN, 6	Absent
»	4 (0.648)	1.40	Hexane, 5	60	1	NQ, 71	DHN, 11	8
THN	4 (0.648)	1.40	Absent	70	1	NQ, 96		Absent
THA	4 (0.848)	1.40	»	80	1	AQ, 5	DHA, 67	28
»	4 (0.848)	1.40	Octanol, 4	90	3	AQ, 49	DHA, 37	Absent
THA*	4 (0.848)	1.56	Absent	60	3	AQ, 33	DHA, 67	»
HQ	4 (0.440)	1.40	Chloroform, 7	45	0.5	BQ, 82		»
»	8 (0.880)	0.70	Chloroform, 5	24	0.5	BQ, 97		»

Note. DDN is 1,4-dihydroxy-5,8-dihydronaphthalene, THN is 4a,5,8,8a-tetrahydronaphthalenedione-1,4, HQ is hydroquinone, BQ is benzoquinone-1,4, NQ is naphthoquinones-1,4, AQ is anthraquinone-9,10, DHN is 5,8-dihydronaphthalenedione-1,4, THA is 1,4,4a,9a-tetrahydroanthraquinone-9,10, DHA is 1,4-dihydroanthraquinone-9,10.

*In experiment, 25 ml of 0.25 M $H_9PMo_6V_6O_{40}$ (HPA-6) (or 6.25 mmol) was used.

Diene synthesis with the simultaneous oxidation of the adducts was carried out in the same set-up. Before the experiment, the reaction mixture was heated to the necessary temperature, and air was replaced from the flask by blowing gaseous 1,3-butadiene. During the reaction, which was carried out under intense mixing, 1,3-butadiene was continuously admitted into the reactor from the gas chamber. The

reaction products were isolated similarly to the procedure described for the experiments on oxidative dehydrogenation. The results of experiments are shown in Table 2.

The solutions of reduced HPA-*x* (H_m HPA-*x*) after removing the reaction products were oxidized with dioxygen (regenerated) and used multiply.

TABLE 2

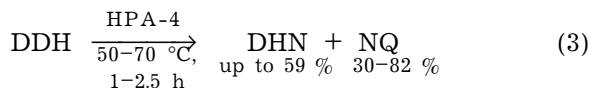
Results of experiments on condensation of hydroquinone (HQ) and naphthoquinone-1,4 (NQ) with 1,3-butadiene in the presence of aqueous solution of 0.25 M of $H_9PMo_6V_6O_{40}$ (HPA-6) (reaction time was 10 h in all the experiments)

Substrate (S)	Charging				T, °C	Yield, %			
	S, mmol (g)	HPA-6, ml (mmol)	HPA : S molar ratio	Solvent, ml		AQ	DHA	THA	NQ
HQ	5 (0.550)	25 (6.25)	1.25	Chloroform, 5	23		1	23	71
»	5 (0.550)	25 (6.25)	1.25	Trichloethylene, 5	23		2	46	47
»	5 (0.550)	25 (6.25)	1.25	Absent	23	9	3	67	15
»	5 (0.550)	25 (6.25)*	1.25	»	23	10	4	65	17
»	5 (0.550)	50 (12.5)	2.5	»	23	19	9	45	21
»	5 (0.550)	50 (12.5)	2.5	»	40	19	4	49	22
NQ	4 (0.632)	25 (6.25)	1.56	»	23	54	19	4	20

*Acid salt of HPA-6 of the composition $NaH_8PMo_6V_6O_{40}$ was used in the experiment.

RESULTS AND DISCUSSION

Oxidative dehydrogenation of DDN in the presence of 0.25 M HPA-4 ($H_7PMo_8V_4O_{40}$) proceeds at 50–70 °C with the yield of NQ from 30 to 82 % and DHN up to 59 % (Scheme (3)). An increase in reaction temperature causes an increase in the yield of NQ (see Table 1):

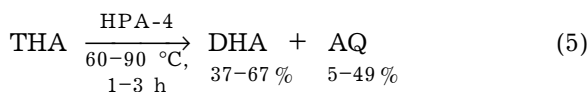


It is remarkable that this reaction can be carried out without the phase of organic solvent. Before start of mixing, the substrate in the solid state is introduced into the thermostated solution of HPA-*x*. The initial substrate may be the adduct (THN) itself and not the product of its isomerization (DDN). The yield of NQ observed in this case was even higher and accounted for 96 %. No DHN was detected in the reaction mixture (see Table 1):

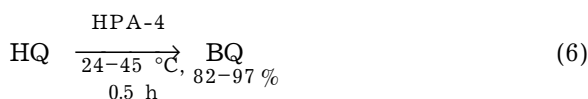


It follows from the data obtained that the known [3, 10] preparative method of obtaining NQ (see Scheme (2)) requiring preliminary isomerization of THN into DDN and its oxidation in two stages, at first into DHN and then into NQ using two different oxidizing agents, can be substantially simplified and carried out catalytically in the presence of HPA-*x* solution.

We established that the oxidative dehydrogenation of THA (see Table 1) in the presence of HPA-4 requires more severe conditions than dehydrogenation of THN and DDN:



Quite the contrary, oxidation of HQ into BQ occurs very easily (catalytically) even at room temperature with a high yield (up to 97 %); temperature rise decreases the yield of BQ:

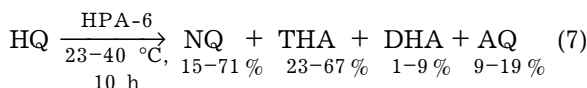


High acidity of HPA-*x* solutions (pH ~ 0=1), as well as good oxidative properties exhibited by them in the oxidative dehydrogenation of various substrates, allowed us to choose HPA-*x*

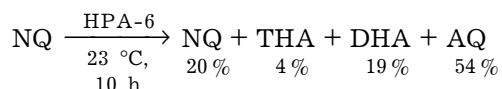
as catalysts for sequential performance of two reactions in a single operation: Diels = Alder condensation of the substrates with 1,3-butadiene, followed by oxidation of partially hydrogenated adducts. It was reported that HPA were used as acid catalysts in diene synthesis [11]. For instance, condensation of NQ with 1,3-butadiene according to Diels – Alder in toluene in the presence of phosphorus-tungsten HPA of Keggin structure $H_4PW_{12}O_{40}$ deposited on silica gel, as well as its cerium and cesium salts, was described in [12, 13]. The yield of THA was 70–80 %. Since P – W – HPA and their acid salts do not exhibit oxidative properties, oxidation of adducts into AQ was not observed. With Mo–V-phosphorus HPA-*x* used, we have strong oxidizing agents because redox potentials of completely oxidized HPA-*x* solutions are about 0.9–1.0 V.

At present, methods of obtaining HQ are being mastered; in particular, starting from phenol and 1,4-diisopropyl benzene [14], which will allow obtaining cheaper HQ and using it as the initial compound in the synthesis of 1,4-quinones of naphthalene and anthracene series. We showed that it turned out to be possible to start from HQ and achieve its complete oxidation into BQ in the presence of HPA-6 of the composition $H_9PMo_6V_6O_{40}$, then carry out BQ condensation with 1,3-butadiene and oxidize the adducts into AQ (Scheme (7), see Table 2). The addition of the second 1,3-butadiene molecule is likely to require higher temperature. To achieve more complete oxidation of partially hydrogenated products into AQ, higher HPA-*x* concentration is necessary, because the oxidative potential of solutions decreases while the reactions proceed according to Scheme (7) due to the reduction of V(V) atoms into V(IV).

Not only HPA-*x* but also their acid salts, the solutions of which also have low pH, are active in the reactions proceeding according to Scheme(7). The results for the sodium salt of HPA-6 $NaH_8PMo_6V_6O_{40}$ as a catalyst are listed in Table 2. The yields of products in the presence of this salt are close to those for HPA-6 itself:



Condensation of NQ with 1,3-butadiene and oxidation of adducts under the same conditions (see Table 2) proceeds to a higher extent: for NQ conversion of 80 %, the yield of AQ reaches 54 %:



CONCLUSIONS

The results obtained provide the evidence that Mo–V–phosphorus heteropolyacids heteropoly acids (HPA-*x*) are promising as efficient catalysts for the oxidation by dioxygen of the adducts of diene synthesis of 1,4-benzo- and 1,4-naphthoquinones with butadiene into 1,4-quinones of naphthalene and anthracene series. Catalysts based on HPA-*x* exhibit high proton acidity and are also active at the stage of diene synthesis. They allow this stage to be carried out at low temperature and without high pressure. Realization of the two stages in one reactor without isolating the intermediate products provides a new efficient route for the synthesis of 1,4-naphtho- and 9,10-anthraquinones.

In the case of development of a cheap method of synthesis of hydroquinone, it may become promising to synthesize 1,4-naphtho-

and 9,10-anthraquinones from HQ and 1,3-butadiene. These compounds are semi-products for the synthesis of various dyes, and efficient catalysts of delignification of wood cellulose.

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