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INFLUENCE OF PROCESS CONDITIONS ON THE KINETICS  
OF THE LIQUID-PHASE CATALYTIC HYDROGENATION OF  
AROMATIC NITRO COMPOUNDS

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The yield of arylhydroxylamines ArNHOH (intermediate products in the liquid-phase catalytic hydrogenation of aromatic nitro compounds ArNO<sub>2</sub>) is determined [1-3] by the ratio of the rates of hydrogenation of the nitro compound and of the disproportionation (dismutation) of the ArNHOH formed according to the reaction



An increase in the hydrogen pressure leads to an increase in the hydrogenation rate of ArNO<sub>2</sub> but has no effect on the dismutation rate; this increases the yield of the corresponding ArNHOH [3]. The present article presents the results obtained in the investigation of the influence of the pH of the medium, the nature of substituent, and temperature on the above ratio of the reaction rates and on the yield of substituted phenylhydroxylamines.

Data are available in the literature on the hydrogenation of nitrobenzene and its derivatives under different conditions; however, in most cases they are based on measurement of the overall rate of hydrogen absorption (occasionally with additional measurement of the catalyst potential) in the course of several simultaneous reactions, without taking into account the specific characteristics of each of them.

It is usually assumed that a change in the pH of the medium has no significant effect on the hydrogenation of nitro compounds [4]; however, the occurrence of additional interactions between the intermediate products in an alkaline medium is noticed in [5]. Based on the fact that our procedure [3] allows us to determine, besides the overall rate of hydrogen absorption, the distribution of products during the course of the reaction, we were able to study the influence of the conditions used on the rate of each of the reactions occurring in the catalytic hydrogenation of ArNO<sub>2</sub>.

Preliminary tests showed the complex relationship that exists between the process characteristics and the pH of the medium. This can be seen from Fig. 1, which illustrates the distribution of the products during the hydrogenation of p-chloronitrobenzene (PCNB) in the presence of HCl and NaOH. In the first stage of the reaction (the hydrogenation of ArNO<sub>2</sub> to the corresponding ArNHOH) the pH of the medium has no significant effect on the reaction rate. On the other hand, the rate of conversion of p-chlorophenylhydroxylamine (PCPHA) to the amino derivative depends strongly on this factor and increases proportionally with the amounts of acid or alkali added to the reaction mixture. At the same time, the yield of PCPHA decreases.

The following schemes can be postulated for the disproportionation of arylhydroxylamines in the case of acid and base catalysis.

Acid catalysis:

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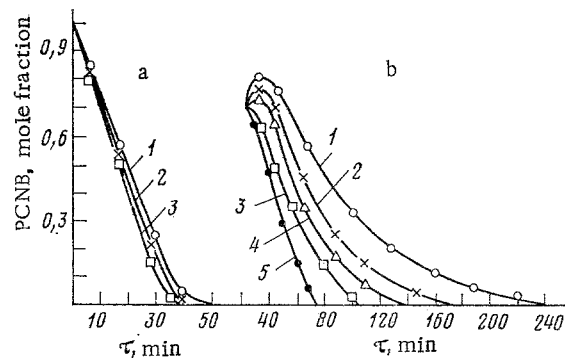
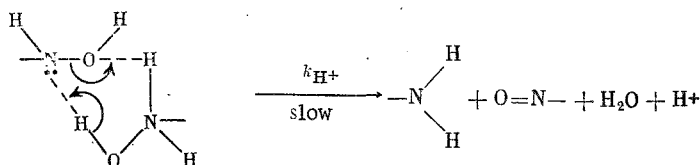


Fig. 1. Effect of the addition of acid and alkali (g-eq/liter) on the hydrogenation rate of PCNB (a) and the disproportionation rate of PCPHA (b) in the presence of a 5% iridium catalyst: 1) without additions; 2) with 0.0038 HCl; 3) 0.0049 NaOH; 4) 0.0076 HCl; 5) 0.0082 NaOH.

TABLE 1. Influence of the Substituent Nature on the Hydrogenation of Substituted Nitrobenzenes in the Presence of a 5% Iridium Catalyst ( $k_a$  and  $k_c$  are the rate constants of the hydrogenation of nitro compounds and the dismutation of arylhydroxylamines, respectively, mole/kg·h)

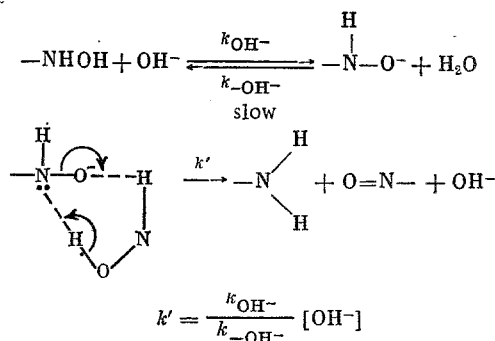
Initial nitro compound	$\sigma_p$ [10]	$k_a$	$k_c$	Maximum yield of arylhydroxylamine, %
p-Nitrophenol	-0,37	50,3	$\rightarrow \infty$	0
p-Nitroanisole	-0,27	116,2	$\rightarrow \infty$	0
p-Nitrophenetole	-0,24	85,9	$\rightarrow \infty$	0
p-Nitrotoluene	-0,17	205,9	8,2	52
Nitrobenzene	0	303,5	12,0	68
p-Nitrobenzaldehyde	0,19	436,5	0	~100
p-Chloronitrobenzene	0,23	373,2	7,9	89
p-Bromonitrobenzene	0,23	256,2	14,9	78
p-Nitrobenzoic acid	0,24	307,8	0,1	~100



The effective rate constant is equal to

$$k = k_{\text{H}^+} [\text{H}^+]$$

Base catalysis:



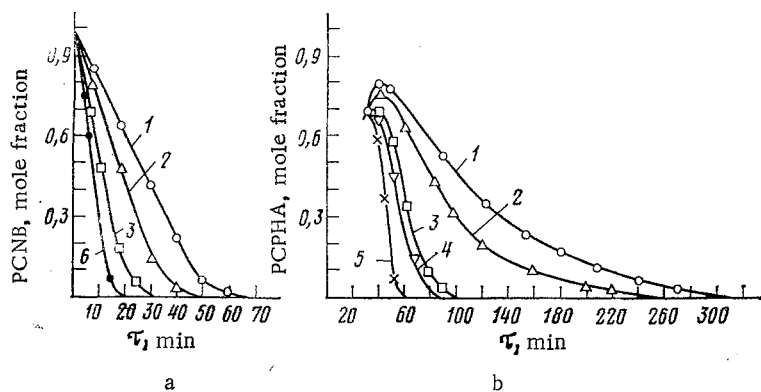


Fig. 2. Influence of the temperature on the hydrogenation rate of PCNB (a) and the disproportionation rate of PCPHA (b) in the presence of a 5% iridium catalyst, °C: 1) 15; 2) 20; 3) 30; 4) 35; 5) 40; 6) 50.

In accordance with the established character of the influence of the pH of the medium, the minimum disproportionation rate and the maximum ArNHOH yield is achieved when the process is carried out in a neutral medium. Evidently, for this reason it is not possible to achieve a quantitative yield of p-alkoxyanilines in the hydrogenation of nitrobenzene in an acidic medium and simultaneous rearrangement of the ArNHOH formed according to Bamberger [6] as this has been suggested in [7, 8].

Earlier measurements of the absorption rate of hydrogen in the hydrogenation of various substituted nitrobenzenes in the presence of different catalysts showed [5, 9] that nitro compounds with electron-donor substituents hydrogenated more slowly than nitro compounds with electron-acceptor substituents. A linear relationship exists between the logarithm of the hydrogenation rate constants and Hammett's substituent constants  $\sigma_p$  [5, 9]. The hydrogenation rate of ArNO<sub>2</sub> as a function of the nature of the substituent, using an iridium catalyst, was analogous to that mentioned in the literature [5].

An investigation of the influence of substituents on the disproportionation rate of ArNHOH showed (Table 1) that the reverse relationship holds for this reaction: electron-donor substituents enhance it, while electron-acceptor substituents inhibit it. For this reason no alkoxy- or hydroxy-substituted ArNHOH were obtained in the hydrogenation of the corresponding nitro compounds, while halogen-, carboxy-, and carbonyl-substituted ArNHOH were obtained with high yields.

An investigation of the effect of temperature on the process showed that the hydrogenation rate of ArNO<sub>2</sub> to ArNHOH is less dependent on the temperature than the disproportionation rate (Fig. 2). Our data gave for the apparent activation energy of the first reaction (for the case of PCNB hydrogenation on a 5% iridium catalyst) a value of 5700 cal/mole and for the disproportionation of PCPHA a value of 13,600 cal/mole. As a result of this, a decrease in temperature leads to an increased yield of ArNHOH. In particular, PCPHA was obtained on a platinum catalyst at -10° with a yield of 68.8%, while at 20° the yield was only 13.6%.

#### EXPERIMENTAL

The investigations were carried out in a Vishnevskii autoclave, equipped with a jacket, at a pressure of 0.7 MPa in isopropanol [Technical Specification (TU) 6-09-402-75, chemically pure]; iridium (IKhF-5, TU 6-02-7-44-74) and platinum (BPL-2.5, TU 6-02-7-99-78) catalysts were used on activated-carbon supports, prepared by reduction with sodium borohydride. The experimental procedure was the same as that described in [3]. Class-A hydrogen was used, containing at least 99.7% hydrogen [All-Union State Standard (GOST) 3022-70].

The initial nitro compounds p-nitrotoluene (MRTU 6-09-6409-69, pure-grade), p-nitroanisole (MRTU 6-09-3965-67, pure-grade), p-nitrophenetole (STU 74-5-28-62, pure-grade), p-nitrotoluene (TU MKhP 2072-49, pure-grade), p-nitrobenzaldehyde (GOST 14049-68, pure-grade), p-chloronitrobenzene (TU MKhP 2169-49, pure-grade), p-bromonitrobenzene (MRTU 6-09-1504-64, pure-grade), and p-nitrobenzoic acid (MRTU 6-09-2759-65, pure-grade) were recrystallized twice from isopropanol; nitrobenzene (GOST 5846-51, pure-grade) was redistilled twice. The

purified compounds had characteristics which corresponded to those in the literature. When investigating the effect of pH, different amounts of hydrochloric acid (GOST 3118-67, pure-grade) and sodium hydroxide (GOST 4328-66) were added to the reaction mixture.

The experimentally determined changes in the concentrations of the initial nitro compounds, arylhydroxylamines, and the corresponding amino products were used to calculate the rate constants for the hydrogenation and disproportionation reactions according to the procedure given in [1, 2].

#### CONCLUSIONS

1. It has been shown that conditions for the liquid-phase catalytic reduction of aromatic nitro compounds have a different effect on the hydrogenation of the nitro compounds to the corresponding arylhydroxylamine and on the disproportionation of the latter with the formation of amines.

2. Contrary to the hydrogenation of the nitro group, the disproportionation rate of the arylhydroxylamines depends to a large degree on the temperature and the pH of the medium. Electron-donor substituents increase the disproportionation rate, while electron-acceptor substituents reduce it.

3. The conditions have been determined at which an increased yield of arylhydroxylamines is obtained in the catalytic reduction of the nitro compounds.

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