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CONVERSION OF N-ARYLHYDROXYLAMINES IN THE PRESENCE OF METAL COMPLEXES AND HETEROGENEOUS CATALYSTS

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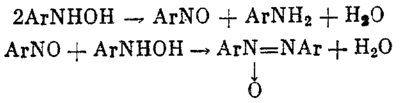
In previous work [1, 2], we showed that N-arylhydroxylamines (ArNHOH) are converted to amines ($ArNH_2$) on heterogeneous catalysts as a result of disproportionation and not of hydrogenation.

It was of interest to study and compare the mechanisms for the conversions, which occur upon the hydrogenation of aromatic nitro compounds ($ArNO_2$) in the presence of homogeneous metal complexes and colloidal catalysts.

The experimental data given in Fig. 1 indicate that there is a similar distribution of reaction components upon using both heterogeneous and homogeneous platinum catalysts. The $ArNO_2$ concentration decreases proportionally to the contact time (τ) and ArNHOH is an intermediate. The ArNHOH content in the reaction mixture initially increases linearly to reach a maximum and then decreases after the complete consumption of $ArNO_2$. The formation of $ArNH_2$ occurs throughout the entire reaction. This nature of the component distribution is a result of the disproportionation of ArNHOH [1-3].

The conversion of ArNHOH to $ArNH_2$ on both catalysts occurs both in the presence of H_2 and in an inert gas atmosphere.

In the presence of a colloidal catalyst, the conversion of ArNHOH in an inert gas atmosphere (Fig. 2) proceeds with the formation of amino and azoxy compounds in the proper stoichiometrical relationship

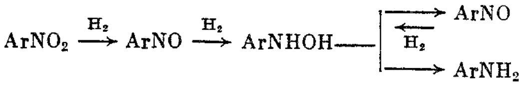


$$2ArNHOH \rightarrow ArNO + ArNH_2 + H_2O$$
$$ArNO + ArNHOH \rightarrow ArN{=}\underset{\substack{\downarrow\\ O}}{N}Ar + H_2O$$

This also indicates the formation of $ArNH_2$ by disproportionation of the corresponding ArNHOH.

A study was carried out on the distribution of the components in the catalytic conversion of $ArNO_2$ alternatively in H_2 and Ar (Fig. 3). The $ArNO_2$ content in segment I, during which the reaction was carried out in H_2, decreases proportionally to τ, which corresponds to the component distribution described above. After replacing H_2 by argon (segment II), the $ArNO_2$ content remains invariant, while the ArNHOH concentration steadily decreases, i.e., ArNHOH is converted to $ArNH_2$ also in the absence of H_2. The subsequent reaction again in H_2 (segment III) features a decrease in the concentration of $ArNO_2$ and increase in the concentration of ArNHOH.

Thus, the reaction upon the hydrogenation of aromatic nitro compounds in the presence of various types of catalysts proceeds through a pathway entailing the catalytic disproportionation of ArNHOH.



$$ArNO_2 \xrightarrow{H_2} ArNO \xrightarrow{H_2} ArNHOH - \begin{cases} \rightleftarrows_{H_2} ArNO \\ \longrightarrow ArNH_2 \end{cases}$$

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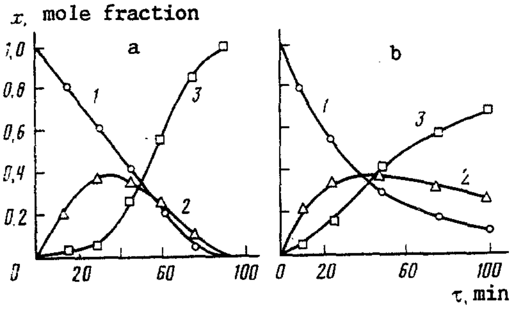

Fig. 1

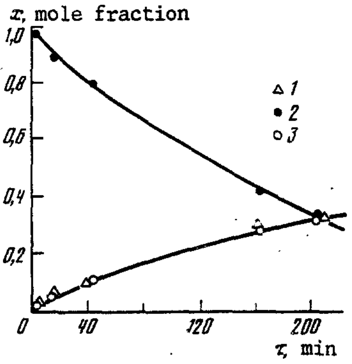

Fig. 2

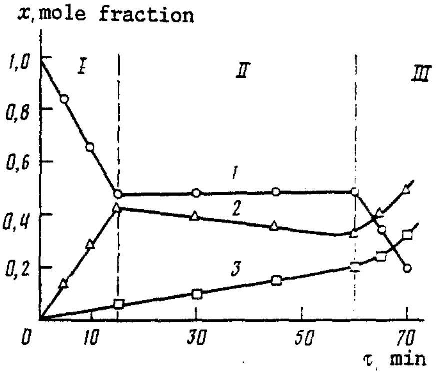

Fig. 3

Fig. 1. Distribution of components upon the hydrogenation of p-chloronitrobenzene at 313 K in the presence of BPL-2.5 platinum catalyst (a) and the complex of Pt(II) with alizarin red S (b): 1) $ArNO_2$, 2) ArNHOH, and 3) $ArNH_2$.

Fig. 2. Distribution of components upon contact of a solution of m-tolylhydroxylamine with a colloidal iridium catalyst in N_2: 1) ArN(O)=NAr, 2) ArNHOH, and 3) $ArNH_2$.

Fig. 3. Distribution of components upon contact of a solution of p-chloronitrobenzene with IKhF-5 iridium catalyst at 313 K alternately in H_2 (segments I and III) and Ar (segment II): 1) $ArNO_2$, 2) ArNHOH, and 3) $ArNH_2$.

EXPERIMENTAL

The study was carried out according to the procedure of Sokol'skii [4] using a thermostatted long-necked hydrogenation flask with 700-800 oscillations per minute. This provided for carrying out the reaction in the kinetic region. IFKh-5 iridium catalyst and BPL-2.5 platinum catalyst supported on activated charcoal were used as the heterogeneous catalysts. The complex of Pt(II) with alizarin red S [5, 6] was used as the homogeneous catalyst. A colloidal iridium catalyst stabilized by polyvinyl alcohol was prepared according to Horn et al. [7].

The method for analyzing the reaction mixture and purification of the starting reagents was analogous to that described in our previous work [1, 2].

Chemically-pure grade 2-propanol was used as the solvent.

The author thanks A. V. Bulatov for providing samples of the metal complex catalyst.

CONCLUSIONS

The nature of the component distribution and the transformations in the catalytic hydrogenation of aromatic nitro compounds are analogous for the use of metal complex, colloidal, and heterogeneous catalysts. The hydrogenation features the formation of amino compounds due to disproportionation of intermediate N-arylhydroxylamines.

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