

3. REDUCTION OF NITROBENZENE IN THE PRESENCE OF THE CHLORIDE COMPLEX OF PALLADIUM SUPPORTED BY SILICA GEL CONTAINING THE γ -AMINOPROPYL GROUP

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Chloride complexes of Pd on silica gels containing amino groups catalyze the hydrogenation of $C=C$, $C\equiv C$, and $C\equiv N$ bonds [1, 2]. We studied the catalytic properties of the Pd complex anchored to silica gel containing the γ -aminopropyl group, in the reduction of nitrobenzene, *m*-dinitrobenzene, phenylhydroxylamine, azoxybenzene, azobenzene, and hydrazobenzene.

EXPERIMENTAL

The Pd complex on silica gel containing γ -aminopropyl groups was obtained from Na_2PdCl_4 according to [2]. A mixture of $1 \cdot 10^{-3}$ mole of substrate in 15 ml of CH_3OH was hydrogenated in the presence of 0.2 g of catalyst ($2 \cdot 10^{-5}$ g-atom Pd), treated with 0.01 g $NaBH_4$, at $20^\circ C$ and atmospheric pressure of H_2 in a long-necked flask with intense agitation (300-400 shakes/min). The purity of the original compounds, according to GLC data was: nitrobenzene (NB) and *m*-dinitrobenzene (*m*-DNB) > 99%; and hydrazobenzene (HB), azoxybenzene (AzOB), azobenzene (AB), and phenylhydroxylamine (PHA) 95-98%. D_2 (98% pure) and CH_3OD (98% pure) were used.

The reaction products were analyzed by a GLC method on an LKhM-8MD chromatograph with a flame-ionization detector at $120-200^\circ C$, using N_2 as the carrier gas, stainless-steel columns 0.75×0.002 m and 2.2×0.002 m, 15% Apiezon L + 1% KOH on Chromaton treated with silane, and an internal standard of pentane.

Mass-spectrographic analyses were conducted on an SN-6 instrument, and IR spectra were taken on a UR-20 spectrometer.

DISCUSSION OF RESULTS

The reduction of NB in the presence of the catalyst under study proceeds for 30 min at a rate of $1.7 \cdot 10^{-2}$ mole/liter \cdot min \cdot g-atom Pd. The reaction is zero order with respect to the substrate [$(3.3-33) \cdot 10^{-2}$ mole/liter] and is first order with respect to H_2 (0.2-1 atm). The process proceeds selectively to aniline. Products of incomplete reduction are not observed. In contrast to this, during the reduction of NB in the presence of a Pd-N-methylpyrrolidone complex up to 9.5% AzOB and 1.5% HB are formed [3].

m-Dinitrobenzene is reduced in steps:



The first NO_2 group of the *m*-DNB is reduced after 10 min, i.e., three times faster than the second group (Fig. 1). The curves of the accumulation and the consumption of *m*-nitroaniline (*m*-NA) are typical for a consecutive process. After the consumption of 3 moles of H_2 , the relative content on the catalyst is: 95% *m*-NA, 2.5% *m*-DNB, and 2.5% *m*-phenylenediamine. The stepwise character of the reduction of *m*-DNB is possibly explained by its more stable coordination in the complex in comparison with *m*-NA. The reduction of *m*-DNB on Pb/C proceeds less selectively: after consumption of 3 moles of H_2 the reaction mixture contains 90% *m*-NA [4].

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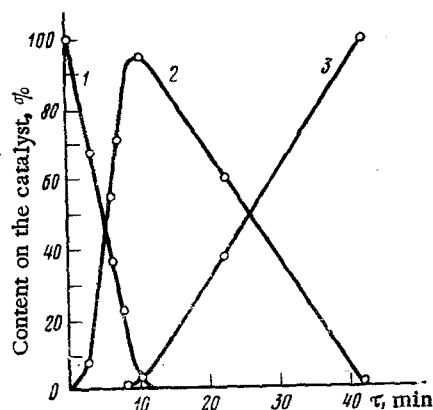
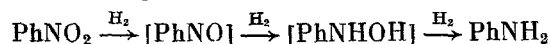


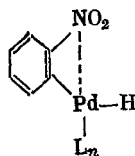
Fig. 1. Reduction of m-dinitrobenzene (1) to m-nitroaniline (2) and m-phenylenediamine (3) on a Pd catalyst.

The hydrogenation of possible intermediate products is studied in order to explain the mechanism of the reduction of NB. It is established that under the investigated conditions, AzOB is selectively hydrogenated to HB; the initial reaction rate is $1.8 \cdot 10^2$ moles/liter \cdot min \cdot g-atom Pd. The reduction of AB to HB proceeds at a rate of $2.2 \cdot 10^2$ moles/liter \cdot min \cdot g-atom Pd. Under these conditions HB is converted to aniline at a rate of 1.2 moles/liter \cdot min \cdot g-atom Pd, which is less than the rate of reduction of NB, AzOB, and AB by a factor of 10^2 . Evidently, the reduction of NB to aniline does not include stages of formation of AzB, AB, and HB. One can assume that the process proceeds according to the scheme



The rate of reduction of PHA to aniline of $1.6 \cdot 10^2$ moles/liter \cdot min \cdot g-atom Pd is close to that of NB. During the stage of the reduction of NB, PHA must be accumulated on the catalyst; however, intermediate products were not observed.

The process probably includes the introduction of Pd along the C-H bond of the aromatic ring with the formation of an intermediate complex



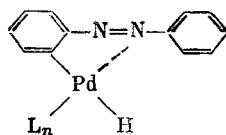
with a σ bond between the Pd atom and the o-C atom of the benzene ring. In this complex the NB is firmly coordinated through a type of chelate and remains in the coordination sphere of the metal until complete reduction of NO_2 to NH_2 , with subsequent rupture of the Pd-C σ bond.

According to this mechanism, the H atom at the ortho position of the aromatic ring takes part in the catalytic reaction. For verification of this supposition, NB was reduced by deuterium in a solution of CH_3OD . There were absorption bands in the IR spectrum of the product in the $2430\text{--}2530\text{ cm}^{-1}$ range which are characteristic for the N-D bond in $\text{C}_6\text{H}_5\text{ND}_2$. According to mass-spectral data, the reduction product has the following distribution regarding masses: 36% 93 ($\text{C}_6\text{H}_5\text{NH}_2$); 50% 94 ($\text{C}_6\text{H}_5\text{NHD}$ or $\text{C}_6\text{H}_4\text{DNH}_2$); 13% 95 ($\text{C}_6\text{H}_5\text{ND}_2$ or $\text{C}_6\text{H}_4\text{DNDH}_2$); and 2% 96 ($\text{C}_6\text{H}_4\text{-DND}_2$). The deficit of deuterium in the aniline obtained is explained by the fact that part of it is exchanged by protium in the reaction with H_2O [5], adsorbed by the carrier of the complex $\text{PhND}_2 + \text{H}_2\text{O} \rightarrow \text{PhNH}_2 + \text{D}_2\text{O}$ or during reaction with free OH groups of the modified silica gel: $\text{PhND}_2 + \text{HO-Si} \rightarrow \text{PhNHD} + \text{DO-Si}$.

After treatment of the product obtained from the reduction of NB by deuterium with an excess of methanol, absorption bands at $2430\text{--}2530\text{ cm}^{-1}$ were present in the IR spectrum, which indicated the almost complete exchange of D by H in the ND_2 group of aniline, and absorption bands at $3360\text{--}3440\text{ cm}^{-1}$, corresponding to N-H vibrations of NH_2 groups, were present. An-

alysis of the product showed the following distribution regarding masses: 72% mass 93, 26% mass 94, and 2% mass 95. The compound with m/e 94 is aniline deuterated in the ring. These data confirm the supposition regarding the participation of a H atom of the aromatic ring in the catalytic reduction of NO₂ groups of NB.

During hydrogenation of AB to HB by deuterium in a solution of CH₃OD in the presence of a Pd complex on the carrier, deuterium is also introduced into the aromatic ring: the amount of the product with a mass of 185 (C₆H₄DNHNHC₆H₅) was 47% in the HB obtained. Evidently, in this case the reaction also proceeds through the formation of a complex of the chelate type



Analogous Pd complexes with AB, benzyldeneaniline, and N,N-dialkylbenzylamine are described in [6].

CONCLUSIONS

1. In the presence of a supported chloride complex of Pd, nitrobenzene is selectively reduced in CH₃OH at 20°C and 1 atm H₂ to aniline without the formation of products of incomplete hydrogenation.
2. The reduction of the NO₂ group of nitrobenzene proceeds through the formation of an intermediate complex with a σ bond between the metal atom and the ortho-C atom of the benzene ring.
3. The supported complex catalyzes the stepwise reduction of m-dinitrobenzene to m-phenylenediamine: after the consumption of 3 moles of hydrogen, m-nitroaniline is formed with a yield of 95%.

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