CATALYTIC ACTIVITY OF METAL COMPLEXES FIXED ON A SOLID SUPPORT. 4. HYDROGENOLYSIS OF CHLOROBENZENES IN THE PRESENCE OF PALLADIUM CHLORIDE COMPLEX DEPOSITED ON MODIFIED SILICA GEL

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Under the influence of a palladium complex deposited on γ-aminopropyl-containing silica gel, nitrobenzene is reduced selectively by hydrogen under mild conditions to aniline without the formation of intermediate products [1]. In the present work we studied the hydrogenolysis of chlorobenzenes at this catalyst.

EXPERIMENTAL

The production of the palladium chloride complex on the support, its activation by treatment with sodium borohydride, and the procedure for the catalytic experiments were described in [2]. In the experiment (20°C, 1 atm H_2) we used 0.2 g of the catalyst ($2 \cdot 10^{-5}$ g-atom of Pd), $1 \cdot 10^{-2}$ g ($\sim 2.5 \cdot 10^{-4}$ mole) of sodium borohydride, $1 \cdot 10^{-3}$ mole of the substrate, and 15 ml of methanol. The chlorobenzene (CB), p-dichlorobenzene (p-DCB), o-chlorotoluene (o-CT), o-chloroaniline (o-CA), and o-, m-, and p-chloronitrobenzenes (o-, m-, and p-CNB) had purity higher than 98% according to GLC data. The products were analyzed by GLC on an LKhM-8MD chromatograph with a flame-ionization detector and with nitrogen as carrier gas. The hydrogenolysis products from CB, o-CT, and p-DCB were analyzed on a stainless-steel column (1 m × 3 mm, 10% SE-301 liquid phase on Chromosorb W) with propyl- or butylbenzene as internal standard. The products from the reduction of o-, m-, and p-CNB were analyzed at 120°C on a steel column (1 m × 2 mm) with Apiezon L (15% + 1% KOH) on silylated Chromaton.

DISCUSSION OF RESULTS

In the presence of the deposited palladium complex the initial rate of elimination of chlorine from chlorobenzene at 20°C and 1 atm H_2 is ∼3 mole/liter·min·g-atom Pd. With the addition of 1 mole of sodium hydroxide to 1 mole of CB the reaction rate increases to 55 mole/liter·min·g-atom Pd. The addition of an excess of alkali (CB:NaOH = 1:5) does not lead to an increase in the rate. In the presence of sodium hydroxide the reaction has zero order in H_2 (0.2-1 atm) and in the substrate ($7\text{-}35 \cdot 10^{-2}$ M).

The introduction of o-CH_3 or p-Cl into the benzene ring of CB did not lead to a significant change in the reaction rate. (In both cases the chlorine elimination rate amounted to 50 mole/liter·min·g-atom Pd). Both chlorine atoms in p-DCB are eliminated at the same rate, and removal of the second chlorine atom only begins after the content of CB in the catalysis product has reached 35-40%. The o-NH_2 group increases the rate of elimination of chlorine twofold (110 mole/liter·min·g-atom Pd) compared with CB. The presence of the O^- substituent in the benzene ring (m-$NaOC_6H_4Cl$) greatly retards the hydrogenolysis (20 mole/liter·min·g-atom Pd). The highest reaction rate (200 mole/liter·min·g-atom Pd) was observed with the o-NO_2 group in the aromatic ring, where the elimination of chlorine is accelerated by four times compared with CB.

The transformation of o-CNB takes place in stages in two directions: 1) removal of chlorine; 2) reduction of the nitro group followed by conversion of NB and o-CA into aniline (3) and (4).

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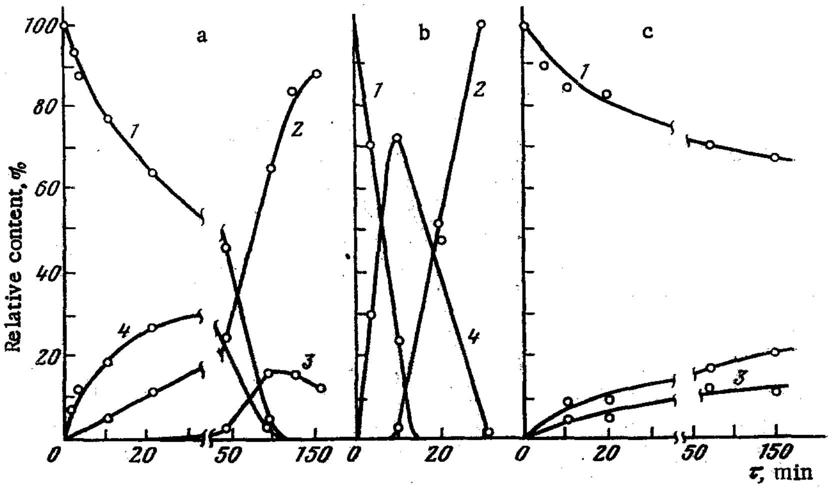
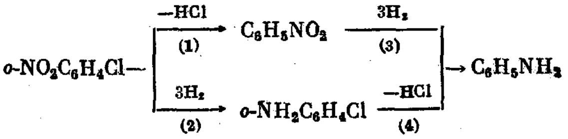


Fig. 1. The transformation of o-chloronitrobenzene at a deposited palladium catalyst in the absence of hydrochloric acid and sodium hydroxide (a) and in the presence of 10^{-3} mole of sodium hydroxide (b) and 10^{-3} mole of hydrochloric acid (c): 1) o-chloronitrobenzene; 2) aniline; 3) o-chloroaniline; 4) nitrobenzene.



$$\begin{tikzcd} & C_6H_5NO_2 \arrow[dr, "3H_2"', "(3)"] & \\ o\text{-}NO_2C_6H_4Cl \arrow[ur, "-HCl", "(1)"'] \arrow[dr, "3H_2", "(2)"'] & & C_6H_5NH_2 \\ & o\text{-}NH_2C_6H_4Cl \arrow[ur, "-HCl"', "(4)"] & \end{tikzcd}$$

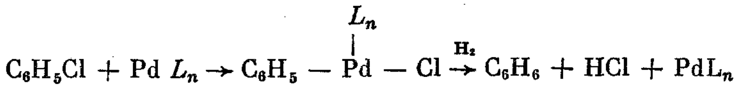
In the absence of sodium hydroxide, o-CNB reacts with the intermediate formation of NB and o-CA (Fig. 1a). In the initial period of the reaction (∼20 min) only NB (up to 27%) and aniline (12%) are formed from o-CNB by reactions (1) and (3). Subsequently the process occurs in both directions, and o-CA is formed in addition to NB. The maximum content of o-CA in the product (17%) is obtained after 100 min, and it then decreases as a result of removal of chlorine according to reaction (4). In the reduction of o-CNB the pH of the medium decreases from 8 at the beginning of the reaction to 5 at the end. Increase in the acidity of the medium changes the direction of the transformation of o-CNB and gives rise to a process with stage character, as was confirmed by further experiments on the reduction of o-CNB in the presence of sodium hydroxide and hydrochloric acid.

In the presence of alkali (NaOH:o-CNB = 1:1) the rate of reaction (1) increases sharply. After 10 min the relative content of NB in the catalysis product amounts to 73% (Fig. 1b). The NB is then soon reduced to aniline. Under these conditions the NO_2 group in o-CNB is not reduced; o-CA was not found in the reaction products. The high selectivity of the process with respect to hydrogenolysis of o-CNB cannot be explained by the effect of the kinetic factor, since the rate of removal of chlorine from CB is three times lower than the rate of reduction of the NO_2 group in NB. The o-CNB probably combines more firmly with the deposited palladium complex than NB, and this gives rise to the consecutive character of the process. An analogous sequence of removal of chlorine and reduction of the NO_2 group is observed in the reduction of m- and p-CNB.

During the reduction of o-CNB with additions of hydrochloric acid (HCl:o-CNB = 1:1) the direction of the transformation changes, and the overall rate of the process decreases. Initially o-CA and aniline are formed, but NB was not found in the product (Fig. 1c). Thus, the direction of the transformation of o-CNB depends on the acidity of the medium; in the presence of alkali the initial reaction is hydrogenolysis of o-CNB (1) with the formation of NB, while in an acidic medium the NO_2 group is reduced initially (2).

This change in the direction of the reaction could be attributed to destruction of the complex catalyst in the acidic medium and to the release of metallic palladium, which (according to [3]) leads the process in direction (2)—(4). However, if the reaction is first carried out in an acidic medium (up to 20% conversion) and then in an alkaline medium (with the addition of an excess of sodium hydroxide), the reduction of the NO_2 group is stopped, and the removal of chlorine soon begins with subsequent reduction of the NB into aniline. This confirms that the complex nature of the catalyst is retained in the acidic medium.

It can be supposed that the hydrogenolysis of Cl includes the stage of oxidative addition with the formation of an intermediate arylmetal σ complex and subsequent cleavage of the Pd—C bond with the release of HCl and regeneration of the catalyst:



$$C_6H_5Cl + Pd\,L_n \rightarrow C_6H_5 - \overset{\overset{\displaystyle L_n}{|}}{Pd} - Cl \xrightarrow{H_2} C_6H_6 + HCl + PdL_n$$

Analogous σ complexes have been obtained by the reaction of Pd(0) with aromatic chlorine compounds [4].

During the hydrogenolysis of Cl the stage of the formation of the σ complex with palladium is evidently controlling. Polarization of the C—Cl bond should accelerate the reaction. In fact, the presence of a strong electron-withdrawing substituent (the NO_2 group) in the aromatic ring considerably increases the rate of removal of chlorine. The electron-donating substituent O^- greatly reduces the hydrogenolysis rate.

The formation of the σ complex depends to a significant degree on the acidity of the medium. In the presence of acid oxidative addition of the palladium at the H—Cl bond probably occurs readily [5] with the formation of a hydride complex of the $HPdClL_n$ type, not capable of forming a σ complex with o-CNB and catalyzing the removal of Cl but catalyzing the reduction of the NO_2 group. When the reaction is carried out in a basic medium, the released HCl is neutralized by alkali, and the removal of chlorine is not retarded.

CONCLUSIONS

1. The palladium chloride complex deposited on γ-aminopropyl-containing silica gel catalyzes the hydrogenolysis of chlorobenzenes at 20°C and 1 atm H_2.

2. The direction of the transformation of o-chloronitrobenzene varies, depending on the acidity of the medium. In the presence of sodium hydroxide the removal of chlorine occurs initially, and in the presence of hydrochloric acid the NO_2 group of chloronitrobenzene is reduced first.

3. The hydrogenolysis of the chlorine atom in the presence of the metal complex catalyst presumably includes a stage of oxidative addition at the C—Cl bond to form an intermediate arylmetal σ complex.

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