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STUDY OF THE CATALYTIC ACTIVITY OF METAL COMPLEXES ATTACHED TO A SOLID SUPPORT. 6. REDUCTION OF NITROBENZENE AND ITS HALOGENATED DERIVATIVES BY CHEMICALLY BOUND HYDROGEN IN THE PRESENCE OF IMMOBILIZED Rh COMPLEXES

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Rh complexes attached to modified silica gels catalyze the reaction of hydrogen transfer from 2-propanol (P-2) to cyclohexanone, styrene, allylbenzene, and cyclohexene-2-one [1]. It was previously found [2] that triphenylphosphine complexes of Rh and Ru are active in the reaction of reduction of nitrobenzene (NB) by 2-propanol. It is known that complex hydrides, NaBH, in particular, are also used for reduction of NB on metal complexes [3].

The catalytic properties of Rh complexes immobilized on silicagels containing amino groups and aminophosphine groups in reduction of NB and different halonitrobenzenes by transfer of hydrogen from P-2 and NaBH, were investigated in the present study.

EXPERIMENTAL

Synthesis of the silica gels with grafted amino (γ -AMPS) and aminophosphine (γ -AMPPS) groups and immobilization of Rh complexes on them were conducted according to [4] (Table 1). Attachment of RhCl₃ on Y-AMPS was conducted in ethanol at room temperature. After complete absorption of the salt, the sample was treated with boiling ethanol. The starting compounds (P-2, NB, hydrazobenzene (HB), azobenzene (AzB), azoxybenzene (AzOB), o-, m-, and p-chloronitrobenzenes (o-, m-, and p-CNB), p-bromonitrobenzene (p-BNB), and p-bromotoluene (p-BT) had a purity $\geq 98\%$ according to the GLC data. (CD₃)₂CDOD and NaBD₄ (98% purity) were used in the experiments. The experiments were conducted in a reactor with a magnetic stirrer equipped with a water jacket, reflux condenser with a hydroseal, and a device for taking samples. The reactor was filled with 0.04-0.07 g of catalyst [(3.2-8.7) ·10⁻⁶ g ·atom Rh], the system was evacuated and filled with Ar or H₂ previously purified of O₂ impurities, and 5 ml of the solvent and the promotor (solution of KOH in P-2) were added. NaBH4 was added to the reactor together with the catalyst. The reaction mixture was stirred for 15 min, heated to the required temperature, and the support was added $[(6.4-17.4)\cdot 10^{-6} \text{ mole}]$. The products of the reaction were analyzed by GLC on a Biokhrom-21 chromatograph with a flame-ionization detector at 120-200°C, N₂ carrier gas, 2 m \times 3 mm stainless steel column, XE-60 (5%) liquid phase on Chromaton N-AW. AzB and HB were not separated in these conditions of analysis. The activity of the catalysts was characterized by the value of the initial rate of transformation of the substrate W°, mole/g atom Rh min. The mass spectrometric analysis was conducted on a Varian MAT-311A.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 534-539, March 1989. Original article submitted November 11, 1987. TABLE 1. Reduction of Nitrobenzene by 2-Propanol (a) and Sodium Borohydride (b) in the Presence of Immobilized Rh Complexes. $(3.2-8.7)\cdot10^{-6}$ l-g atom Rh, $(6.4-17.4)\cdot10^{-5}$ mole NB, 10 ml P-2, Ar; a) [KOH] = $(25.6-69.6)\cdot10^{-3}$ mole/liter, 82.4°C; b) $(25.6-69.6)\cdot10^{-5}$ mole NaBH₄, 50°C

Catalyst*	Immobilized ~ complex	Concentra- tion of Rh, mole/g·10 ⁵	Hydrogen donor	W ⁰ ·10, mole/g· atom Rh·min
(I)	$[RhCl(COD)]_2$	6,2	P-2 NaBH4 NaBH4	3,8 45,3 36,2 **
(11)	RhCl (PPh ₃) 3	4,5	P-2 NaBH₄	0,1 40,0
(III)	RhCl ₃	6,4	P−2 NaBH₄	0,2 29,9
(IV)	$[RhC](COD)]_2$	6,3	P-2 NaBH	6,2 39,0
(V)	RhCl (PPh3) 3	8,5	P-2 NaBH₄	0,1 36,7
(VI)	RhCl₃	22,3	P-2 NaBH4	0,1 32,9

*(I)-(III): on γ-AMPPS, (IV)-(VI): on γ-AMPS. **Experiment in 2-methyl-2-propanol.



Fig. 1. Effect of [KOH] (1) and the amount (G) of NaBH₄ (2) on W^o in the presence of (I) $(3.2 \cdot 10^{-6} \text{ g'atom Rh}, \text{[NB]} = 6.4 \cdot 10^{-5} \text{ mole}, 10 \text{ ml P-2}, 82.4 ^{\circ}\text{C}).$

RESULTS AND DISCUSSION

Reduction of NB by transfer of hydrogen from P-2. Metal complexes (I)-(III) and (VI) do not catalyze reduction of NB and (V) is not very active in an atmosphere of H_2 in a solution of P-2 (82.4°C). Sample (IV) decomposes in these conditions with formation of metallic Rh. In Ar medium, none of the heterogeneous metal complexes (HMC) exhibited catalytic activity. A different picture was observed on addition of KOH to the reaction mixture. After treatment with the alkali, HMC catalyzed reduction of NB by transfer of hydrogen from P-2.

$$PhNO_2 + 3i-C_3H_7OH \xrightarrow{Cat} PhNH_2 + 3(CH_3)_2CO + 2H_2O .$$

The color of the samples changed from light yellow to dark brown.

As Fig. 1 shows, the dependence of W° on [KOH] is extreme, and the maximum value of $W^{\circ} = 4.0 \cdot 10^{-1}$ mole/g·atom Rh°min is attained with 25.6·10⁻³ mole/liter; the subsequent decrease in W° is probably due to partial decomposition of HMC. In the absence of Rh complexes, KOH does not reduce the NO₂ group.

In the presence of (II), (III), (V), and (VI), promoted by the alkali, W° has similar but low values. Only (I) and (IV) exhibited relatively high activity in the reaction of hydrogen



Fig. 2. Effect of [NB] on W^o in the presence of (I) $(3.2 \cdot 10^{-6} \text{ g·atom Rh}, 82.4^{\circ}\text{C}, 24.8 \cdot 10^{-5} \text{ mole NaBH}_4, 10 \text{ ml P-2}).$



Fig. 3. Reduction of azoxybenzene (a) and m-chloronitrobenzene (b) in the presence of (I): a) $6.4 \cdot 10^{-5}$ mole AzOB: 1) AzOB, 2) AzB and HB, 3) AN; b) $6.4 \cdot 10^{-5}$ mole m-CNB: 4) m-CNB, 5) m-CAN, 6) AN; $3.2 \cdot 10^{-6}$ g·atom Rh, $24.8 \cdot 10^{-5}$ mole NaBH₄, 10 ml P-2, 82.4°C.

transfer to the NO₂ group. This difference in the catalytic activity is apparently due to the effect of the functional group of the support.

The temperature of the process has an important effect on the catalytic properties of the synthesized HMC. When the temperature is increased from 60 to 82.4°C, the reaction rate increases by approximately one order of magnitude, while the change in W° is insignificant at lower temperatures.

The rate of reduction of NB is a function of the concentration of the hydrogen donor, P-2. In dilution of P-2 with 2-methyl-2-propanol (1:10), W° decreases by 8.6 times (in comparison to reduction in P-2), and the reaction does not take place in general in a solution of 2-methyl-2-propanol.

The set of data obtained suggest that reduction of NB in the presence of HMC promoted by an alkali takes place according to a scheme similar to the one proposed in [1] for reduction of the carbonyl group in ketone. The rate of reduction of NB is 2.5 times lower than for cyclohexanone. This is probably due to the fact that three entries of the P-2 molecule in the coordination sphere of the complex is required for reduction of NB. We note that no products of incomplete reduction of NB were found in the reaction mixture.

<u>Reduction of NB by transfer of hydrogen from sodium borohydride.</u> In the absence of a catalyst, NaBH₄ does not reduce NB (P-2, 82.4°C). As Table 1 shows, all HMC exhibit high catalytic activity when treated with NaBH₄ in a solution of P-2 and are in the following order with respect to the rate of transformation of NB into AN: (I) > (II) $\stackrel{\sim}{\sim}$ (IV) > (V) > (VI) > (III). The differences in the activity are comparatively small. When NaBH₄ is used as a hydrogen donor, the nature of the immobilized compound and functional group of the support apparently affects the catalytic properties of the metal complexes in reduction of the NO₂ group to a small degree.

TABLE 2. Reduction of Halogen-Substituted Nitrobenzenes on (I) (3.2-8.7)·10⁻⁶ g·atom Rh, (6.4-17.4)·10⁻⁵ mole support, (25.6-69.5)·10⁻⁵ mole NaBH₄, 10 ml P-2, Ar, 82.4°C

	W ⁰ ·10*, mole/g·atom Rh·min		
Support	a	Ъ	
p-BNB p-CNB o- CNB m-CNB	8,8 12,0 10,8 14,8	3,5 1,1 0.2 1,4	

*Rate of formation (a) and dehalogenation (b) of halogen-substituted anilines.

The rate of reduction of NB by sodium borohydride in 2-methyl-2-propanol differs little from W^o in P-2 (Table 1). This indicates that a complex hydride is primarily the hydrogen donor in reduction of the nitro group of NaBH₄ in P-2. The reaction rate increases linearly with an increase in the amount of NaBH₄ in the reaction mixture from $3.2 \cdot 10^{-5}$ to $25 \cdot 10^{-5}$ mole, and the increase in the activity of the catalyst subsequently slows (Fig. 1). When [NB] increases from $3.2 \cdot 10^{-3}$ to $38.4 \cdot 10^{-3}$ mole/liter, W^o decreases from $28 \cdot 10^{-1}$ to $10.4 \cdot 10^{-1}$ mole/g. atom Rh·min (Fig. 2). This is probably due to the formation of inactive forms of the catalyst due to its complexing with NB and the products of the process.

The reduction of some possible intermediate products, AzOB and HB in particular, was studied to elucidate the mechanism of the reaction. It was found that (I) catalyzes reduction of AzOB with a rate of $22.1 \cdot 10^{-1}$ mole/g.atom Rh.min. It is transformed by stages: AzB and HB initially accumulate in the catalyzate, and AN begins to be formed when their concentration in the reaction mixture attains 23-25% (Fig. 3a). HB undergoes hydrogenolysis at the N-N bond with W⁰ = $7.8 \cdot 10^{-1}$ mole/g.atom Rh.min. The rate of reduction of NB is significantly higher in these conditions. Since no intermediate compounds were found in the catalyzate, it is possible to state that NB and the products of its incomplete reduction remain in the coordination sphere of the metal until NO₂ is totally transformed into NH₂. This course of the process is apparently due to the formation of a σ complex of the chelate type as a result of incorporation of Rh at the C-H bond of the aromatic ring. In this complex, the support is strongly coordinated with the Rh atom. Organometallic compounds of this type are described in [5].

The data obtained in reduction of NB by sodium borodeuteride in $(CD_3)_2CDOD$ medium are in good agreement with this hypothesis. The analysis showed that the product of reduction has the following distribution by weight: 96 11.8%, 95 47.1%, 94 100%, 93 82.4%, 92 11.8%, 68 7.1%, 67 34.1%, 66 25.9%, 65 23.5 % (% of intensity of the maximum peak). The presence of the peak of a molecular ion with m/z 96 $(C_6H_4DND_2^+)$ in the mass spectrum indicates the presence of AN deuterated in the nucleus.

Based on the results obtained and the literature data, the scheme of reduction of NB by sodium borohydride can be represented as follows: 1) formation of mono- and dihydride attached complexes of Rh as a result of the reaction of NaBH₄ with HMC [6, 7]; 2) coordination of NB; 3) successive reduction of the NO₂ group into a NH₂ group; 4) liberation of AN in the reaction mixture and regeneration of the catalyst. In the presence of O₂ (molar ratio $O_2/Rh = 400$), the rate of the process decreases by ~ 3 times. If we assume that stages (1) or (3) are the limiting stage of the process, then the passivating effect of the O₂ can be attributed to partial oxidation of hydride forms of Rh. Conducting the reaction in an atmosphere of H₂ has almost no effect on the rate of reduction of NB.

<u>Reduction of chloro- and bromonitrobenzenes by sodium borohydride</u>. Incorporation of a halogen in the benzene ring results in a decrease in the reaction rate (Table 2). Incorporation of Br has the strongest effect. The position of the substituent affects the rate of reduction of the nitro group: the rate of transformation of o-CNB into o-CAN is 1.4 times lower than the rate of transformation of m-CNB into m-CAN.

Dehalogenation can also take place together with reduction of the NO₂ group in the conditions selected. The possible pathways of transformation of the starting halonitrobenzene are represented by the scheme



Hydrodehalogenation of the starting compound did not take place: no NB was found in the catalyzate. This indicates that the reaction takes place in direction (1) and (2). The process takes place selectively: in reduction of p- and m-CNB and p-BNB in the presence of (I), haloanilines are formed with a 100% yield. After completion of the process, splitting of the halogen begins, and AN is formed (Fig. 3b). The rate of dehalogenation of CAN is one order of magnitude lower than the rate of reduction of the NO₂ group, and the bromine derivative undergoes dehalogenation two times more rapidly than the chlorine derivative. A slightly different picture is observed in reduction of o-CNB: splitting of chlorine begins after \sim 35% transformation of o-CNB into o-CAN, and the initial rate of dehalogenation of o-CAN is \sim 50 times lower than the rate of reduction of the NO₂ group. However, after total conversion of o-CNB (the catalyzate contains 94% o-CAN and 6% AN), the rate of cleavage of Cl from o-CAN increases by five times).

The reduction of the NB-p-BT mixture was studied to determine the cause of the selective reduction of halonitrobenzene compounds. It was found that the rate of reduction of NB does not change in the binary mixture, but the rate of transformation of p-BT decreases by \sim 30 times (in comparison to the rate of transformation of the individual supports). After total conversion of NB into AN, the rate of hydrodehalogenation of p-BT increases sharply. NB is apparently more strongly coordinated with the immobilized Rh complex than p-BT, which also causes the consecutive character of reduction of the halonitrobenzene compounds.

The rate of cleavage of the halogen decreases sharply with a decrease in the temperature of the reaction. For example, in the presence of (I) at 25°C, m-CNB undergoes 100% conversion after 30 min with formation of 96.5% m-CAN and 3.5% AN, after which the composition of the catalyzate does not change. A similar picture was observed when (VI) was used.

CONCLUSIONS

1. Rhodium complexes [(RhCl (COD)]₂, RhCl(PPh₃)₃, and RhCl₃ immobilized on silica gel modified by amino and aminophosphine groups catalyze selective reduction of nitrobenzene into aniline in Ar medium (25-82.4°C) by transfer of hydrogen from 2-propanol (KOH promotor) and sodium borohydride.

2. The rate of reduction of nitrobenzene by sodium borohydride is one to two orders of magnitude higher than with 2-propanol.

3. Incorporation of a halogen in the benzene ring results in a decrease in the rate of reduction of the nitro group. Reduction of halonitrobenzenes by sodium borohydride takes place in two stages: The NO₂ group is reduced first, and the halogen is then cleaved.

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