1648 Russian Chemical Bulletin, Vol. 44, No. 9, September, 1995

Catalytic reduction of aromatic polynitro compounds
1. Hydrogenation of 3,5-dinitrophenyl phenyl ether

*D. P. Zakharychev, E. F. Litvin, and V. Z. Sharf**

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

The liquid-phase catalytic hydrogenation of 3,5-dinitrophenyl phenyl ether to give 3,5-diaminophenyl phenyl ether in the presence of Group VIII metals as catalysts has been investigated. The main kinetic characteristics of the process have been established. The reduction occurs *via* the formation of 5-amino-3-nitrophenyl phenyl ether. In terms of their activity, the catalysts studied can be arranged in the following sequence: 1 % Pd/Sibunit > 2 % Pd/C > Lindlare Pd > 5 % Ru/Sibunit > Raney Ni. The selectivity of the process with respect to intermediate 5-amino-3-nitrophenyl phenyl ether depends on the relative adsorption abilities of mono- and dinitro compounds. A promoting effect of water during hydrogenation of 3,5-dinitrophenyl phenyl ether in isopropanol or 1,4-dioxane has been noted. Catalytic synthesis of 3,5-diaminophenyl phenyl ether has been carried out for the first time.

Key words: 3,5-dinitrophenyl phenyl ether; hydrogenation; Pd, Ru, and Ni catalysts; 5-amino-3-nitrophenyl phenyl ether; 3,5-diaminophenyl phenyl ether.

Hydrogenation of aromatic polynitro compounds is the basis of industrial syntheses of monomers for the production of polyamides and polyimides as well as the synthesis of heterocyclic compounds. The possibility of selective hydrogenation of one or two nitro groups of a polynitro compound, while the other groups remain intact, is of particular interest.

The purpose of the present work has been to study hydrogenation of the previously unknown 3,5-dinitrophenyl phenyl ether* to give 3,5-diaminophenyl phenyl ether in the presence of catalysts based on Group VIII metals.

Experimental

Freshly prepared solvents of "chemically pure" grade were used. The Raney nickel catalyst was prepared by leaching a Ni—Al alloy (1 : 1) with a 20 % solution of KOH. When working with palladium catalysts, samples of POUB-2 (2 % Pd/C) and IKT-23 (1 % Pd/Sibunit) industrial catalysts or Lindlare catalyst ([6 % Pd + 3 % Pb]/$CaCO_3$) were used. The 5 % Ru/Sibunit catalyst was prepared according to the known procedure.[1] Hydrogenation was carried out in a static system, *viz.*, a temperature-controlled two-long-necked flask at an atmospheric pressure of hydrogen and with intense stirring (800 vib. min^{-1}). The solvent (30 mL), dinitro compound (0.1—0.77 mmol), and the catalyst ($(0.4—10) \cdot 10^{-3}$ g of the metal) were placed in the reactor.

The rate of hydrogen absorption was measured and samples for chromatographic analysis were withdrawn during the reaction. The data on the hydrogen absorption were reduced to the normal conditions with allowance for the water vapor pressure.

GLC analysis was carried out on an Avtokhrom-89 chromatograph with a flame ionization detector and a steel column (300×3 mm) packed with 5 % XE-60 on Chromaton HMDS (the 0.2—0.16 mm fraction) using nitrogen as the carrier gas, v = 33 cm^3 min^{-1}; the temperature of the evaporator and the detector was 230 °C, and the initial temperature of the column was 175 °C. After the peaks of the reference compound (triphenylcarbinol) and dinitro compound appeared, the temperature was increased to 220 °C.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 P spectrometer with respect to tetramethylsilane.

3,5-Dinitrophenyl phenyl ether (3,5-DNPPE). M.p. 176 °C. ^1H NMR ($(CD_3)_2CO$), δ: 7.13 (dm, H-8); 7.33 (tm, H-10); 7.49 (tm, H-9); 8.09 (d, H-2); 8.71 (t, H-4). ^{13}C NMR ($(CD_3)_2CO$), δ: 113.24 (C-4); 118.65 (C-2); 121.07 and 126.81 (C-8 and C-10); 131.59 (C-9); 150.46 (C-3); 155.75 (C-5); 160.36 (C-1).

5-Amino-3-nitrophenyl phenyl ether (ANPPE). ^1H NMR ($(CD_3)_2CO$), δ: 5.84 (br.s, NH); 6.65 (dd, H-6); 6.89 (dd, H-2); 7.07 (d, H-8); 7.17 (m, H-10); 7.27 (dd, H-4); 7.40 (dd, H-9). ^{13}C NMR ($(CD_3)_2SO$), δ: 99.35, 102.79, 108.20 (C-2, C-4, C-6); 119.37 (C-8); 124.06 (C-10); 129.88 (C-9); 149.51 (C-3); 151.05 (C-5); 155.42 (C-7); 158.36 (C-1).

3,5-Diaminophenyl phenyl ether (3,5-DAPPE). ^1H NMR ($(CD_3)_2SO$), δ: 4.85 (br.s, NH); 5.44 (d, H-2); 5.60 (t, H-4); 6.93 (d, H-8); 7.04 (t, H-10); 7.33 (t, H-9). ^{13}C NMR ($CDCl_3$), δ: 96.24 (C-2); 96.84 (C-4); 119.10 (C-8); 122.97 (C-10); 129.48 (C-9); 148.66 (C-3); 156.95 (C-1); 159.26 (C-5).

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* 3,5-Dinitrophenyl phenyl ether was kindly provided by S. A. Shevelev and M. D. Dutov (N. D. Zelinsky Institute of Organic Chemistry of the RAS).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1716—1719, September, 1995.

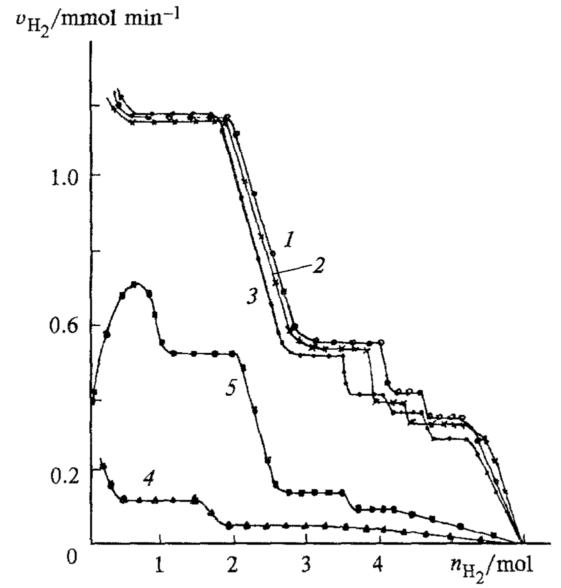

Fig. 1. Dependence of the rate of hydrogen consumption (v_{H_2}) during hydrogenation of 3,5-DNPPE on the amount of H_2 absorbed (n_{H_2}) at a concentration of the starting ether, C_0/mol L^{-1}: 0.05 (in isopropanol) (*1*); 0.75 (in isopropanol) (*2*); 0.3 (in isopropanol in the presence of 0.03 mol L^{-1} of 3,5-DAPPE) (*3*); 0.34 (in dioxane) (*4*); 0.34 (in a dioxane—water mixture, 9 : 1) (*5*). Here and in Figs. 2—4: POUB-2 (0.02 g) as the catalyst, T = 55 °C, p = 1 atm.

Results and Discussion

The kinetic curves of hydrogenation of 3,5-DNPPE in isopropanol (Fig. 1, curves *1—3*) have complex shapes: in the first step of the process, until three moles of H_2 are absorbed, they correspond to the zero order of the reaction with respect to the compound being hydrogenated, and then the rate of the process dramatically decreases. In the second step, the section of the curve corresponding to the zero order is less clearly defined. The rate of the reaction and the shapes of the kinetic curves do not change when the initial concentration of the starting dinitro compound varies (C_0 = 0.05 to 0.75 mol L^{-1}), which indicates that the reaction has zero order with respect to the substrate.

Chromatographic analysis of the catalysate has shown that the nitro groups in 3,5-DNPPE are reduced successively, *i.e.*, the reaction involves intermediate formation of ANPPE (Fig. 2), which was isolated and identified. The selectivity of the formation of ANPPE in the presence of palladium catalysts is 79—85 %. The second step affords 3,5-DAPPE in a high yield (90—92 %).

The activation energies (E_a) of hydrogenation of the first and the second nitro groups of 3,5-DNPPE calculated for the 25—55 °C temperature range are 32±2 and 38±2 kJ mol^{-1}, respectively. The E_a values obtained are in agreement with those reported for hydrogenation of 2,4- and 2,5-dinitrotoluenes in the kinetic region in alcoholic solutions in the presence of a Pd catalyst (E_a = 32 to 42 kJ mol^{-1}).[8]

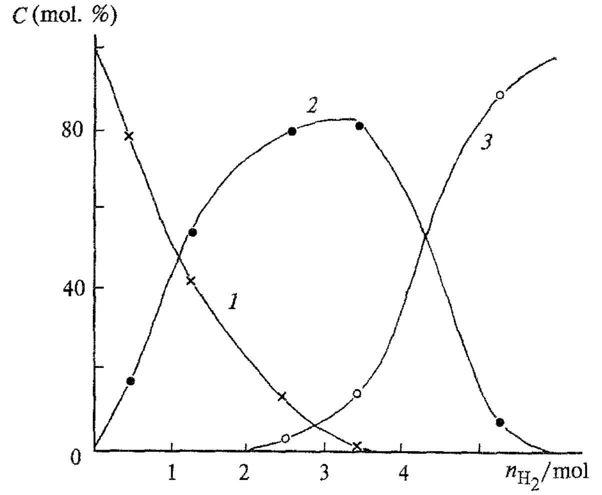

Fig. 2. Variation of the composition of the catalysate during hydrogenation of 3,5-DNPPE (C_0 = 0.25 mol L^{-1}) in isopropanol: 3,5-DNPPE (*1*); ANPPE (*2*); 3,5-DAPPE (*3*).

The high selectivity of the successive reduction of the two nitro groups of 3,5-DNPPE, like the selectivity of hydrogenation of dienes[2] and stable nitroxyl biradicals,[3] is probably explained by the adsorption displacement of the intermediate aminonitro compound by the starting 3,5-DNPPE. To confirm this assumption, we carried out a series of experiments on hydrogenation of binary mixtures of mono- and dinitro compounds: 3,5-DNPPE—nitrobenzene, ANPPE—1,3-dinitrobenzene. Components of the binary mixtures of dinitro compounds (1,3-dinitrobenzene and 3,5-DNPPE) are reduced simultaneously, while in the binary mixtures of mono- and dinitro compounds, the latter are reduced selectively (Fig. 3). Based on the results of the experiments with binary mixtures, we calculated the ratio between the adsorption coefficients of 3,5-DNPPE (b_1) and ANPPE (b_2): b_1/b_2 = 6.2.

The dependence of the specific activities and selectivities of the catalysts studied in the hydrogenation with respect to ANPPE are presented in Table 1. In terms of their specific activities (per g of metal), the catalysts can be arranged in the following sequence: 1 % Pd/Sibunit > 2 % Pd/C > Pd Lindlare catalyst > 5 % Ru/Sibunit > Raney Ni. It is noteworthy that the activity of Pd catalysts depends on the nature of the supporting material. The Sibunit-deposited palladium is the most active. This supporting material differs from activated coal by its macrostructure, *viz.*, predominance of large pores and mesopores.[4] The activity of the Ru catalyst is two orders of magnitude lower than that of the Pd catalysts. The Ru catalyst exhibits as well the lowest selectivity (75 %).

In a number of papers[5—7] it has been reported that water has a promoting effect on hydrogenation of both the aromatic rings[6] and the nitro groups in various nitro compounds[5,7] in the presence of palladium and nickel catalysts. When 3,5-DNPPE was hydrogenated in an

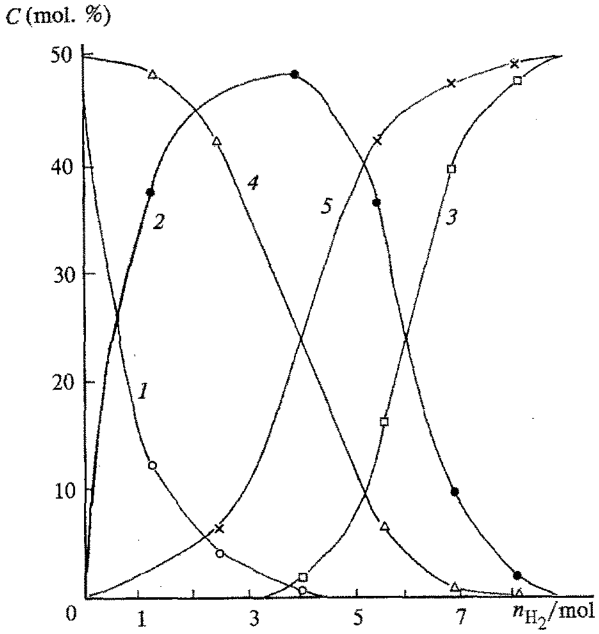

Fig. 3. Variation of the composition of the catalysate during hydrogenation of a mixture of nitrobenzene and 3,5-DNPPE in isopropanol: 3,5-DNPPE (*1*); ANPPE (*2*); 3,5-DAPPE (*3*); nitrobenzene (*4*); aniline (*5*).

Table 1. Dependence of the specific activity of the catalyst in hydrogenation of the first and second nitro groups (w_1 and w_2, respectively) of 3,5-DNPPE and of the selectivity (*S*) with respect to the formation of ANPPE on the nature of the catalyst

Catalyst	w_1*	w_2*	*S* (%)
POUB-2 (2 % Pd/C)	275.0	80.0	85
IKT-23 (1 % Pd/Sibunit)	780.0	350.0	79
Lindlare Pd ([6 % Pd+3 % Pb]/$CaCO_3$)	48.3	10.0	89
5 % Ru/Sibunit	3.4	3.3	75
Raney Ni	1.1	0.6	82

* In mmol (min g_M)$^{-1}$.

isopropanol—water mixed solvent, we found that the addition of up to 4.5 mol. % water to isopropanol results in a dramatic increase in the reaction rate, and as the concentration of water in the solvent is further increased, the reaction rate decreases (Fig. 4). When 3,5-DNPPE is dissolved in mixed solvents containing >40 mol. % water, its suspension is formed. If hydrogenation is carried out in aprotic solvents (1,4-dioxane), addition of water (10 mol. %) exerts an even more pronounced effect (the rate of the reaction increases by a factor of five).

The effect observed was used in the development of a method for preparing 3,5-DAPPE by catalytic hydrogenation of 3,5-DNPPE in aqueous alcohols. Preliminary experiments have shown that using 3,5-DAPPE as a monomer makes it possible to obtain polyimides with enhanced properties.

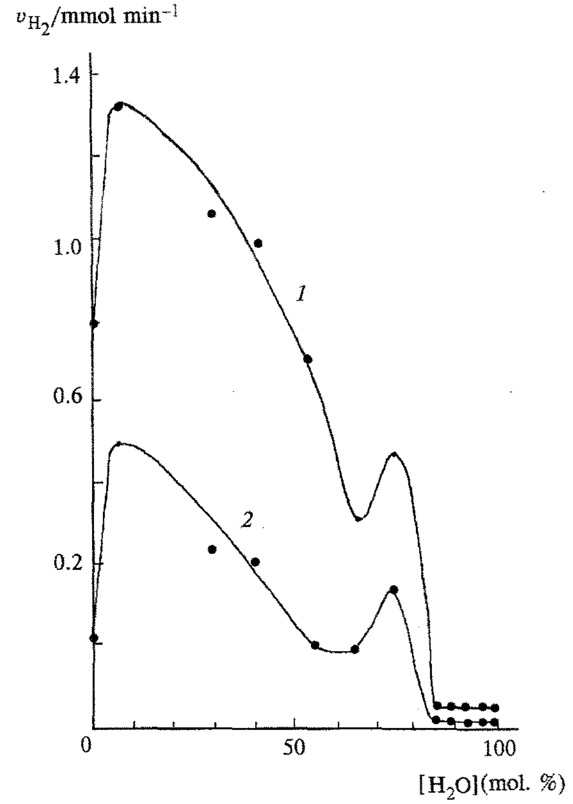

Fig. 4. Dependence of the rate of hydrogen absorption (v_{H_2}) during hydrogenation of the first (*1*) and the second (*2*) nitro groups in 3,5-DNPPE on the concentration of water in aqueous isopropanol.

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Received December 5, 1994