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Effect of Substituents on Nitrobenzene Reduction in the Presence of a Platinum Catalyst

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Abstract—The effect of substituted nitrobenzene structure on the kinetics of their catalytic reduction in propanol-2 in the presence of a platinum catalyst is studied. The reaction order with respect to a nitro compound changes in the series of the studied substrates. A satisfactory correlation between the apparent rate constants for the reaction and the E_{LUMO} values of the substrates is observed for several nitro compounds.

INTRODUCTION

The structure of a substrate is one of the main factors that determine both the reactivity of aromatic nitro compounds (NC) in hydrogenation and process regularities.

The aim of this work was to study the effect of certain substituents on both the rate and mechanism of the reduction of substituted nitrobenzenes in the presence of an alumina–platinum catalyst. We examined 4-nitroaniline (**I**), 2-amino-4-nitroaniline (**II**), 2-chloro-5-nitroaniline (**III**), 2-chloro-4-nitroaniline (**IV**), 2-bromo-4-nitroaniline (**V**), 3-nitroaniline (**VI**), 4-nitrophenol (**VII**), nitrobenzene (**VIII**), 2,6-dichloro-4-nitroaniline (**IX**), and 3-nitrochlorobenzene (**X**) as substrate nitro compounds.

The reduction of a nitro group of halogen-containing aromatic substrates may be accompanied by a side hydrodehalogenation reaction. Earlier, we studied the influence of different factors on the rate and selectivity of 2-chloro-4-nitroaniline reduction on platinum and palladium catalysts with various metal concentrations [1]. The maximum selectivity was achieved when the process was carried out in propanol-2 with a 0.5% Pt/Al_2O_3 catalyst. This alumina–platinum catalyst and the solvent were used to study the influence of the substrate structure.

EXPERIMENTAL

Experiments were carried out in propanol-2 in a Vishnevskii autoclave (200 cm^3) equipped with a jacket with a constant-temperature liquid along with stirring under hydrogen pressure. The reaction mixture volume was 100 cm^3. In the course of the experiment, the pressure in the autoclave was kept constant using a receiver system. The catalyst was obtained by γ-Al_2O_3 impregnation with chloroplatinic acid as described in [2]. Before use, the catalyst was ground and fractionated using appropriate sieves to separate the fraction with particle size within $(50–250) \times 10^{-9}$ m. Nitro compound reduction was controlled by hydrogen consumption. The volume of hydrogen was measured with a calibrated burette and by GLC. When a desirable value of hydrogen consumption degree was attained, a sample of the reaction mixture was withdrawn, filtered to remove the catalyst, and analyzed to determine the reaction products. The concentrations of the initial nitro compounds were determined with a Khrom-4 chromatograph equipped with a flame-ionization detector (a 1 m × 3 mm column, SKTFT-50Kh on Chromaton N–AW). The apparent rate constants for hydrogenation were calculated from the nitro compound concentrations that changed in the course of the reaction. The concentration of the corresponding phenylhydroxylamine (PHA) was determined by the potentiometric titration of a sample using a sodium nitrite solution as described in [3]. Azo and hydrazo compounds, which were formed in the reactions between intermediates [4], were identified by IR and UV spectroscopy on Specord M80 and Specord M400 instruments. Quantum chemical calculations were performed using the MOPAC 6.0 program package.

RESULTS AND DISCUSSION

In the preliminary experiments, we determined the conditions for the kinetics control of the reduction of compounds **I**–**X** and studied the effect of the catalyst particle size on the reduction rate. The rate is at maximum and remains unchanged for a particle sizes less than 150×10^{-9} m. The rate of reduction of these compounds changes linearly with a catalyst concentration ranging from 2.0 to 10 g/l in agreement with the first order with respect to a substrate. An increase in the stirring velocity from 1600 to 2800 rpm does not change the kinetic parameters of the process. The Arrhenius plot is linear for all the compounds at 293–333 K. Taking into account our preliminary results, we chose the following conditions to study the effect of substituted nitrobenzene structure on the kinetics of catalytic reduction: propanol-2 as a solvent; 313 K; hydrogen pressure, 2.0 MPa; the initial concentration of a nitro compound, 0.35 mol/l; 0.5% Pt/Al_2O_3 as a catalyst (6.0 g/l) with a particle size of $(50–80) \times 10^{-9}$ m; and stirring velocity, 2800 rpm. The reaction temperature of 313 K ensures a satisfactory rate and selectivity of the process (the hydrodehalogenation degree during the reduction of halogen-containing nitro compounds was lower than 0.5–0.7%).

Figure 1 illustrates the effect of the nitro compound structure on the shape of the curves of hydrogen consumption. Analysis of reaction mixtures showed that the reduction of nitro compounds **I**–**VII** is not accompanied by the accumulation of nitrozo or arylhydroxylamine derivatives or condensation by-products. Figure 2a presents our results for 2-chloro-4-nitroaniline hydrogenation. When studying the effect of the hydrogen pressure on the reaction rate, we found that the reduction of compounds **I**–**VII** has zero order with respect to hydrogen at 1.5–4.0 MPa. The true reaction order with respect to substrates **I**–**VII** was determined to be first from the dependence of the initial rate on the nitro compound concentration. Taking into account the same catalyst concentration in the experiments, the rate law for the hydrogenation of these nitro compounds is $w = k[NC]$. The same mechanism of nitro compound reduction is confirmed by the shapes of the curves of hydrogen consumption: the hydrogenation occurs with a constantly decreasing rate up to the consumption of the theoretically required amount of hydrogen (Fig. 1, curves *1*–*7*).

Electron transfer from a catalyst to adsorbed molecules resulting in the formation of a radical anion is very likely during the hydrogenation of aromatic nitro compounds [5]. Generally, nitro compound reduction occurs via a complex mechanism including the formation and protonation of radical anions [6, 7]. According to published data, the hydrogenation of aromatic nitro compounds is usually controlled by electron transfer from a catalyst metal atom to the LUMO of substrates. In the above case, we suggested to use the LUMO energies of the studied substrates to theoretically describe the reactivity of nitro compounds. The quantum chemical calculation of relevant characteristics was performed by the AM-1 method. A satisfactory correlation between the apparent rate constants for reduction with the E_{LUMO} values of substrates is observed (Fig. 3). Our data confirm that the reduction of aromatic nitro compounds on heterogeneous catalysts occurs via the radical anion mechanism [8] and that the rate-limiting step in the reduction of aromatic nitro compounds **I**–**VII** is the electron transfer from the occupied *d* orbitals of the platinum atom to the unoccupied π*-orbitals of a nitro compound.

Our study of nitrobenzene reduction showed that, from the very beginning of the reaction, the solution contains the final product (aniline), whose concentration increases as the initial nitro compound is consumed, whereas the maximal concentration of the corresponding phenylhydroxylamine is lower than 10%. Figure 2b illustrates how the reaction mixture composition changes during nitrobenzene reduction. Our findings suggest that nitrobenzene reduction occurs via the hydrogenation pathway without a substantial accumulation of intermediates in the reaction solution and on a catalyst. This may be attributed to the fact that phenylhydroxylamine is reduced more rapidly than nitrobenzene. Phenylhydroxylamine formed in the reaction undergoes further reduction to aniline.

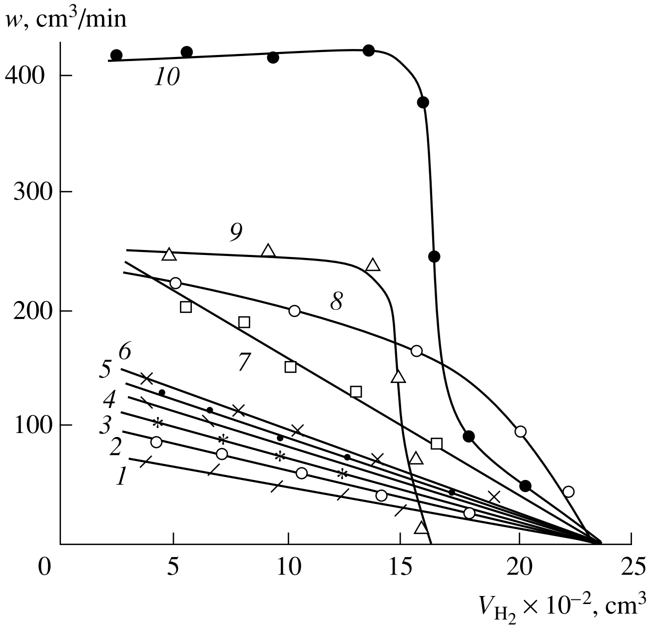

Fig. 1. Effect of the substrate structure on the rate of hydrogen consumption (propanol-2, 313 K, P_{H_2} = 2.0 MPa, $[NC]_0$ = 0.35 mol/l, and [Cat] = 6 g/l): (*1*) 4-nitroaniline, (*2*) 2-amino-4-nitroaniline, (*3*) 2-chloro-5-nitroaniline, (*4*) 2-chloro-4-nitroaniline, (*5*) 2-bromo-4-nitroaniline, (*6*) 3-nitroaniline, (*7*) 4-nitrophenol, (*8*) nitrobenzene, (*9*) 2,6-dichloro-4-nitroaniline, and (*10*) 3-nitrochlorobenzene.

The hydrogenation of 2,6-dichloro-4-nitroaniline and 3-nitrochlorobenzene occurs via different reduction mechanisms. The reaction occurs at a constant rate up to the consumption of 2/3 of the theoretically required concentration of hydrogen followed by a decrease in the consumption rate (Fig. 1, curves *9* and *10*). The results of the potentiometric titration of the reaction mixtures suggest that the reduction of compounds **IX** and **X** involves the formation and accumulation of the corresponding phenylhydroxylamines in the solution (Figs. 2c and 2d). Under the above conditions, 3-nitrochlorobenzene hydrogenation occurs in two steps. First, the reduction results in the formation of intermediate phenylhydroxylamine, the concentration of which increases with substrate consumption and attains a maximum value when ~2/3 of the theoretically

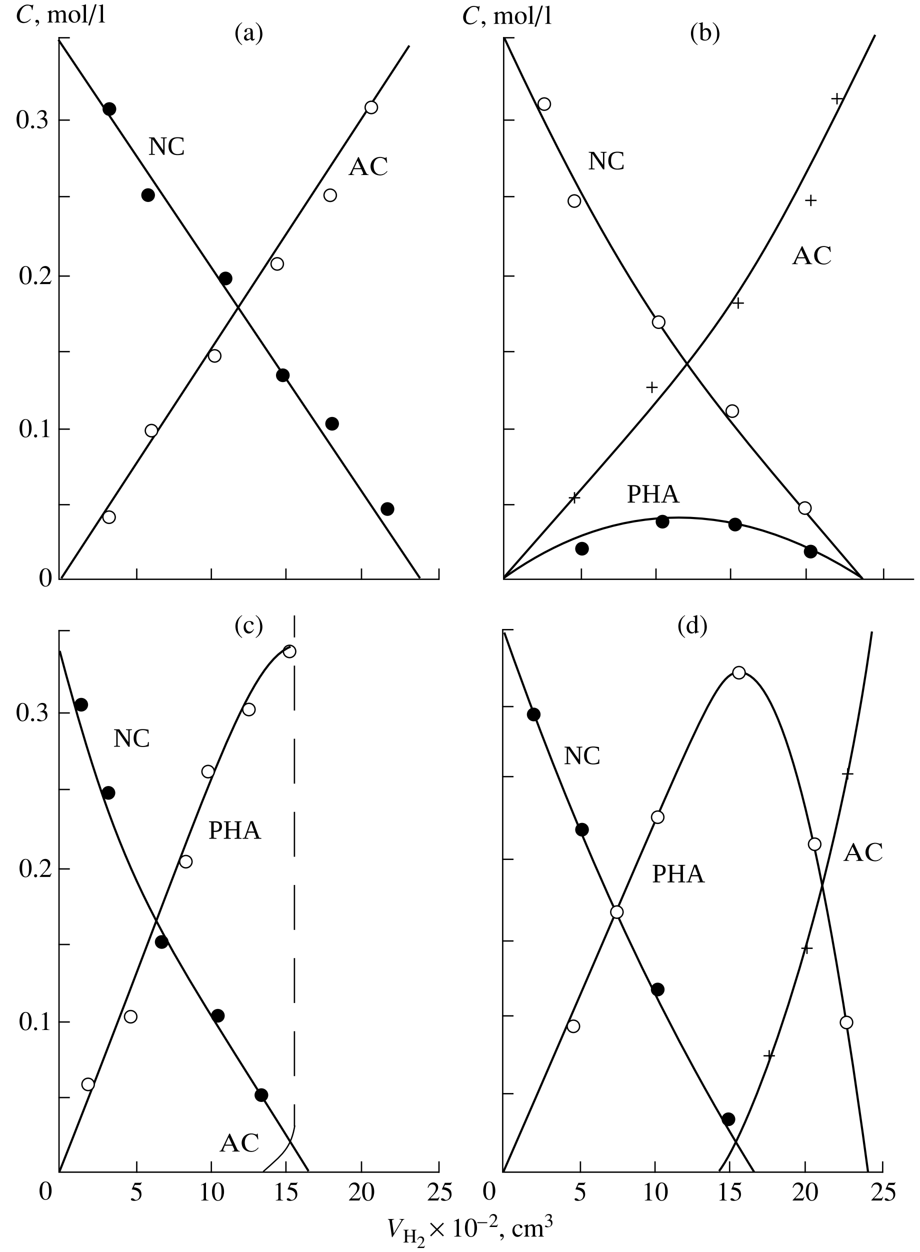

Fig. 2. Reaction mixture composition in the reduction of (a) 2-chloro-4-nitroaniline, (b) nitrobenzene, (c) 2,6-dichloro-4-nitroaniline, and (d) 3-nitrochlorobenzene (for conditions, see Fig. 1).

required concentration of hydrogen is consumed. Phenylhydroxylamine reduction to an amino compound (AC) begins only after the complete consumption of a nitro compound from the reaction mixture. No other intermediate was detected in the reaction mixture. Phenylhydroxylamine transformation into the corresponding diamine during 2,6-dichloro-4-nitroaniline reduction is hampered. This may be due to the higher stability of this intermediate because the electron-acceptor substituents (chlorine atoms) retard dismutation [9]. The yield of resulting 2,6-dichloro-4-hydroxylamino-aniline was 91–93 mol % (T_m = 86–88°C; the concentration of the main compound was 98.9% as determined by potentiometric titration). Found, %: C, 40.30; H, 3.18; Cl, 36.70; N, 14.52. From these data, we calculated the formula $C_6H_6Cl_2N_2O$ with M = 193.29. Calculated, %: C, 40.35; H, 3.16; Cl, 36.73; N, 14.49.

When studying the effect of the **IX** and **X** concentrations, we found that the reaction rate is independent of the initial concentration (0.2–0.8 mol/l) and follows the zero order with respect to a nitro compound. This suggests that hydrogen activation is the rate-limiting step of the reduction of nitro compounds **IX** and **X**.

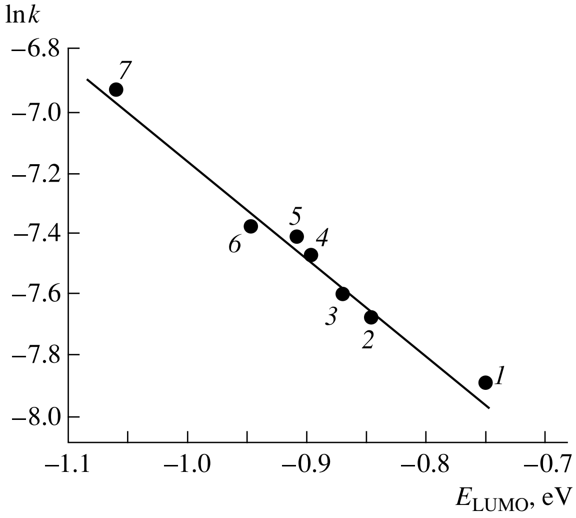

Fig. 3. A plot of ln *k* vs. E_{LUMO} (for conditions, see Fig. 1): (*1*) 4-nitroaniline, (*2*) 2-amino-4-nitroaniline, (*3*) 2-chloro-5-nitroaniline, (*4*) 2-chloro-4-nitroaniline, (*5*) 2-bromo-4-nitroaniline, (*6*) 3-nitroaniline, and (*7*) 4-nitrophenol.

Our findings suggest that the presence of an electron-acceptor substituent (a halogen atom) in the structure of the above compounds determines their high adsorption ability. The initial nitro compound replaces the intermediate phenylhydroxylamine from the surface of a catalyst accumulated in the solution. The presence of an electron-donor substituent (an amino group) retards the reduction and ensures the first reaction order with respect to the substrate. When the substrate molecule contains both the halogen atom and the amino group (nitro compounds **III**–**V**), the reduction mechanism is determined by the amino group.

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