Liquid-phase catalytic hydrogenation of 3,4-dichloronitrobenzene over Pt/C catalyst under gradient-free flow conditions in the presence of pyridine

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Experimental data on nitro compound uptake, the intermediate product accumulation, and the corresponding amine compound generation were obtained on hydrogenating 3,4-dichloronitrobenzene over Pt/C catalyst in the gradient-free flow regime in the presence and absence of pyridine. In addition, a side reaction of dehalogenation was investigated. The role of pyridine admixture on every step of the process was analyzed and the rate of hydrogenation of the nitro compound was determined both in the presence and in the absence of inhibitor.

Key words: liquid phase hydrogenation, catalysis, inhibition, aromatic nitro compounds, gradient-free flow conditions.

Liquid-phase catalytic hydrogenation of chlorine-containing aromatic nitro compounds over heterogeneous catalysts is one of the effective methods for the industrial production of amine compounds applied to the synthesis of pharmaceuticals and chemical protection facilities for plants. The reaction of interest is accompanied by the side reaction of chloride ion elimination that more or less readily proceeds over any known catalyst for hydrogenation. In addition to a decrease in the yield of the target amine product, dehalogenation causes heavy corrosion of the apparatus. Therefore, the research focused on inhibition of dehalogenation is of importance. The rate of chloride ion elimination can be reduced either by selecting the optimal catalyst or by introducing an appropriate admixture into the reaction medium.

Earlier,[1] we showed that with the introduction of pyridine admixture into the reaction medium in catalytic hydrogenation of chlorine-containing aromatic nitro compounds it is possible to effectively inhibit the side reactions of dehalogenation of chlorine-containing amine products. However, the inhibitor affects every step of catalytic hydrogenation of aromatic nitro compounds. Hence, in order to investigate the influence of pyridine explicitly, experimentally found rates of the reactions proceeding in the presence and absence of pyridine admixtures need to be compared. Moreover, the parameters affected by the inhibitor it is nessary to determine.

Earlier we described the effect of pyridine, which was used as an admixture, on the rate of hydrogenation of 3,4-dichloronitrobenzene (3,4-DCNB) as well as on the rate of hydrogenation of the intermediate compound, 3,4-dichloro-*N*-phenylhydroxylamine (3,4-DCPHA), and the amino product, *i.e.* 3,4-dichloroaniline (3,4-DCA).[1] The kinetic experiments were carried out under static conditions at atmospheric hydrogen pressure using the method of the initial rate measurements.[2] It was found that the effect of the inhibitor on the hydrogenation reactions of 3,4-DCNB and intermediate 3,4-DCPHA is not competitive in nature and inhibition of the mentioned reactions is mainly caused by general influence of the inhibitor on the adsorption of hydrogen on catalytic surface.[3] Meanwhile, in the presence of pyridine, the rate of dehalogenation of 3,4-DCA is significantly reduced and molecules of chloroaniline and hydrogen compete to occupy the active cites on the surface of the catalyst.

Under static conditions, hydrogenation process needs to be realized with low conversions (up to 5—7%) of the feed compound.[4] In this case, adsorption of nitro compound and intermediate 3,4-DCPHA is so strong that the ensuing transformation of 3,4-DCA, which is weakly adsorbed on the catalyst, is nearly negligible. The processes of deep conversion are noticeably activated at high conversions of the initial and intermediate products. At enhanced conversions, hydrogenation of nitro compound and transformation of the intermediate product seem to proceed independently with respect to conversion of the generated amine compound. Actually, if the process is performed in a batch reactor, all these reactions proceed simultaneously and interfere with each other. Nevertheless, under static condition these effects are unlikely to be noticed. One can detect these only when the process is investigated in a gradient-free flow reactor. However, when hydrogenation is performed in a flow regime in the presence of highly dispersed catalyst powders, the particles of the catalyst may be washed out from the reactor with the reaction flow. We managed to find the conditions at which

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hydrogenation proceeds without removal of the catalyst from the reactor. The experimental procedure for the performance of hydrogenation of nitro compounds over fine-grained catalysts in the gradient-free flow regime was described earlier.[2]

The purpose of the present study is to reveal features of hydrogenation of 3,4-DCNB under gradient-free flow conditions at atmospheric hydrogen pressure both in the presence and absence of pyridine. It was important to obtain the kinetic data on every step of hydrogenation process, while taking into account that the reactions proceed simultaneously in the presence of heterogeneous catalyst at different conversion of the initial feed compound. The detailed information is hardly obtainable when the experiments are carried out in a static regime. At the same time, in the case of the gradient-free flow regime, all the characteristics of the process are maintained constant and the reaction system is under the steady-state conditions.[3] That is particularly important for heterogeneous reactions. On the other hand, activity and selectivity of the catalyst under the steady-state condition can noticeably be different from the initial parameters, especially in a multistep process. Application of gradient-free flow conditions for the study of such complicated process as hydrogenation of aromatic nitro compounds in the presence of pyridine allows us precisely evaluate the influence of inhibitor on every step of the process in the presence of initial compounds, intermediates, and final products and describe the observed effects using math equations.

Experimental

The procedure for the experiments carried out under gradient-free flow conditions was described earlier.[3] Hydrogenation of 3,4-DCNB was performed in a duck-shaped temperature-controlled shaker reactor at 50±0.2 °C. The rate of hydrogen uptake was independent of the number of shakings (*i.e.* intensity of mixing).[4] The content of nitro compounds, nitroso derivatives, corresponding amine product, and intermediate 3,4-DCPHA in the reaction mixture was determined voltammetrically using three electrode scheme.[5] The content of chloride ion was estimated by potentiometric measurements using mercurimetry technique.

Commercial 3,4-dichloronitrobenzene (Specifications TU-6-01-1005-75) was doubly distilled and doubly recrystallized from isopropanol (after purification, m.p. 39.6 °C, 99.7—99.9%). Isopropanol (reagent grade, Specifications TU-6-09402-75) was used as received. The catalyst was platinum supported on carbon BPL-2.5 (Specifications TU-602-7-99-78) with 2.2±0.2% Pt. The particle size of the catalyst was 80—200 μm. The catalyst (1.00 g) was loaded into the reactor containing 30–35 mL of the solution. Reagent grade pyridine used as the inhibitor was doubly distilled from dry alkali (b.p. 115.5–115.6 °C). Hydrogen (USSR State Standard GOST 3020-80) was applied as a reducing agent.

The starting concentrations of 3,4-DCNB in IPA solution were about 0.41—0.43 mol L^{-1}. Pyridine concentration was about 0.05 mol L^{-1}.

The experimental procedures for hydrogenation performed in the presence and absence of pyridine have a number of differences. In the experiments conducted without inhibitor, the initial solution was directly introduced in the reaction mixture containing the catalyst and nitro compound solution and preliminary hydrogenation of the initially loaded starting nitro compound was not performed. On the contrary, several portions of 3,4-DCNB diluted in IPA and contained inhibitor were consequently reduced using static method untill the constant residual activity of the catalyst was achieved. The obtained solution with the inhibitor was then introduced in the reactor and the process reached steady-state conditions. Application of this procedure significantly reduces the time needed to reach steady state. A decrease in the catalytic activity during the experiment did not exceed 1%.

Under the above described conditions, the hydrogenation process is controlled by internal diffusion. The estimation of the diffusional factors was published earlier.[6]

By varying the feed rate of the starting mixture (w) it was possible to determine the stationary concentrations of the initial compounds and the reaction products at different contact times, which were determined from the equation $K = w[A_0]/g$, where w is the volume feed rate (L h^{-1}), $[A_0]$ is the starting concentration of nitro compound in the reaction mixture (mol L^{-1}), g is the catalyst weight (1.00 g).

Results and Discussions

Figure 1 shows the experimental data describing the effect of the contact time (K) on the relative concentration (C_i/A_0) of 3,4-DCA, 3,4-DCNB, 3,4-DCPHA, and chloride ion at hydrogenation of 3,4-DCNB in the presence and absence of inhibitor.

As it can be seen in Fig. 1, introduction of inhibitor does not change the quantitative composition of the reaction mixture. Nevertheless, as the analysis of the mixture shows, the reactions of chloride ion abstraction proceed with a considerably larger extent in the absence of pyridine. Thus at low values of K, produced aniline undergoes hydrogenation. In the presence of pyridine, monochloroaniline is the main product of dehalogenation and aniline is formed in very small amounts. When K is lower than 0.06 mol g^{-1} h^{-1}, concentration of 3,4-DCPHA is remarkably higher in the presence of pyridine than in its absence (Fig. 2).

The relationship between relative concentration of 3,4-DCPHA and the contact time is described by a volcano-type curve. Moreover, in the presence of pyridine, the peak is observed at lower values of K (0.06—0.07 mol g^{-1} h^{-1}) and the maximum concentration of 3,4-DCPHA is *ca.* 1.3 lower than that observed in the absence of inhibitor. In the range of K from 0.026 to 0.052 mol g^{-1} h^{-1}, concentration of 3,4-DCPHA in the reaction mixture without inhibitor is noticeably lower than the concentration values found in the presence of pyridine admixture. Nevertheless, the maximum concentration of 3,4-DCPHA obtained in the presence of inhibitor is significantly lower. This result can

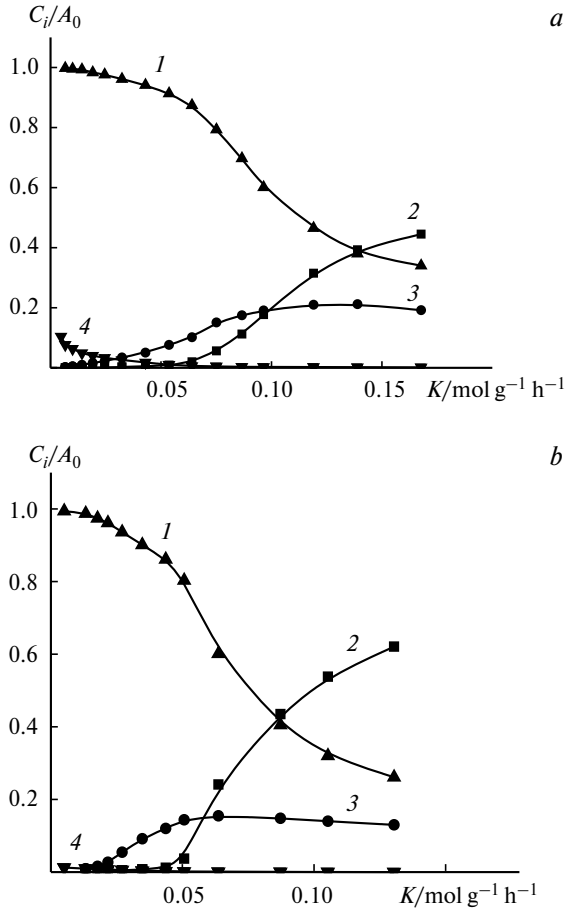


Fig. 1. The relative concentration (C_i/A_0) of the components as a function of the contact time of hydrogenation of 3,4-DCNB in a gradient-free flow reactor in the absence (*a*) and presence of pyridine (*b*): 3,4-DCA (*1*), 3,4-DCNB (*2*), 3,4-DCPHA (*3*), Cl^- (*4*).

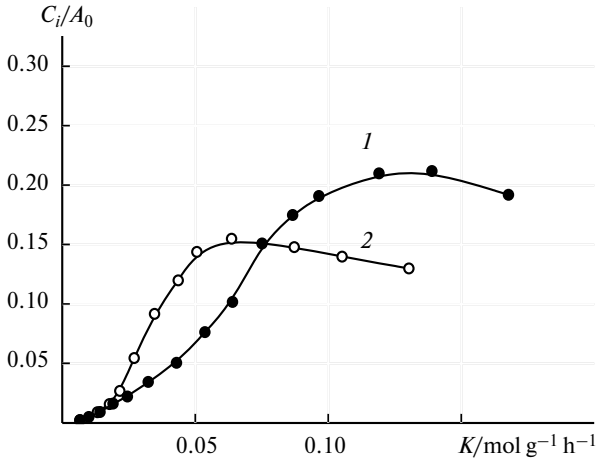


Fig. 2. Relative concentration of 3,4-DCPHA (C_i/A_0) as a function of the contact time in the absence (*1*) and presence of pyridine (*2*).

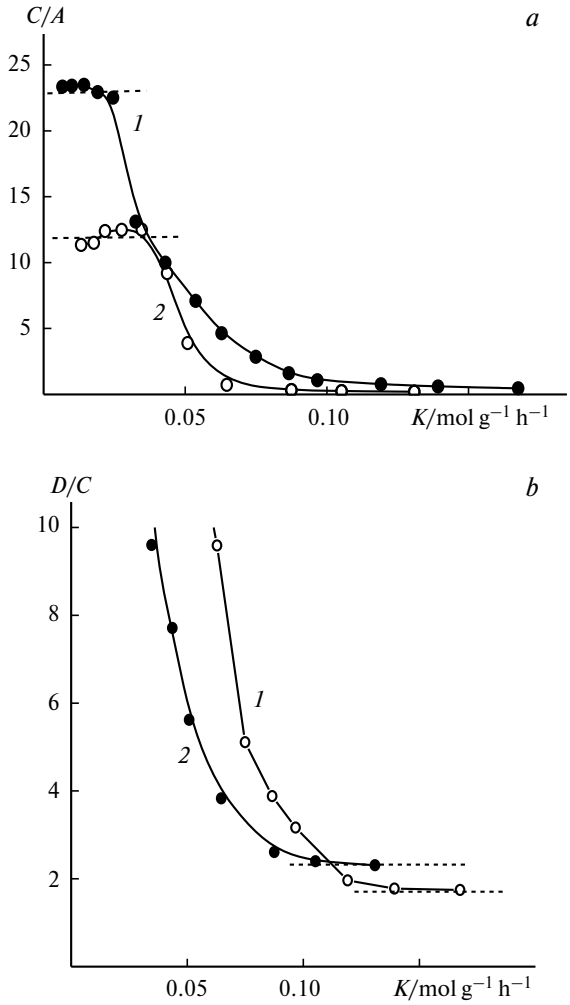


Fig. 3. Relative concentrations of (*C/A*) 3,4-DCPHA and 3,4-DCNB (*a*) and the concentration ratio of (*D/C*) 3,4-DCA and 3,4-DCPHA (*b*) as a function of the contact time in the absence (*1*) and presence of pyridine (*2*).

provide evidence that the passway of the intermediate product consumption in the presence of inhibitor is changed.

Figure 3 illustrates the effect of the contact time on the ratio of concentrations of 3,4-DCPHA to 3,4-DCNB (*C/A*), as well as on that of 3,4-DCA to 3,4-DCPHA (*D/C*).

As shown in Fig. 3, *a*, in the range of *K* from 0.0052 to 0.031 mol g^{-1} h^{-1} the ratio of the stationary concentrations of 3,4-DCPHA and 3,4-DCNB (*C/A*) is nearly constant. In the presence of inhibitor the ratio is 11—12, while without inhibitor it is 21—23. With further increase in the contact time the *C/A* ratio decreases. Moreover, the decrease is more gradual in the presence of pyridine. Such behavior of the concentration ratio of 3,4-DCPHA and 3,4-DCNB is not observed when hydrogenation is carried out under static conditions. The ratio of the stationary concentrations of 3,4-DCA and 3,4-DCPHA (*D/C*) (see Fig. 3, *b*) regularly decreases in the range of *K* from 0.0052

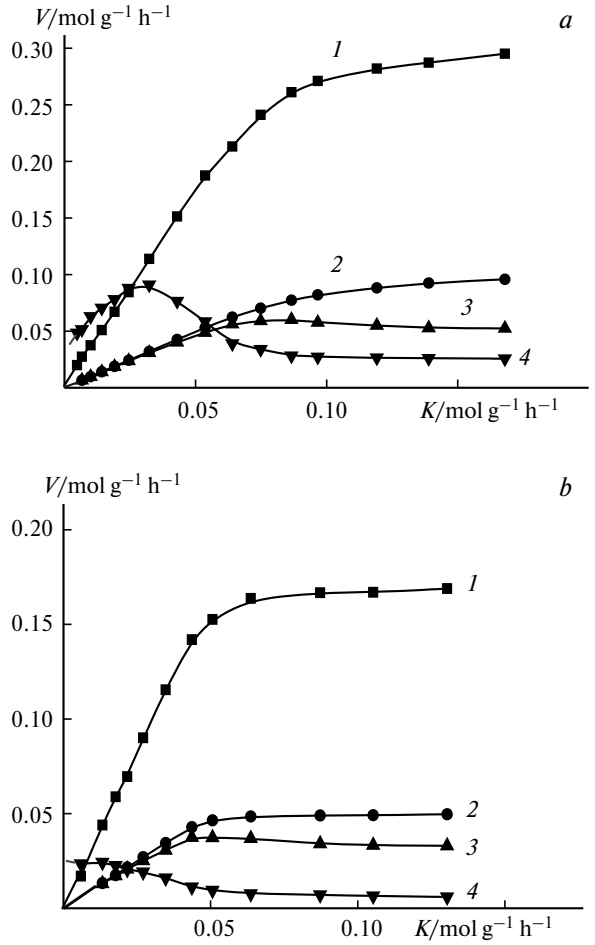


Fig. 4. Dependences of the rates of uptake of H_2 (*1*) and 3,4-DCNB (*2*) as well as accumulation of 3,4-DCA (*3*) and chloride ion $[Cl^-] \cdot 10^2$ (*4*) on the contact time in the absence (*a*) and presence of the inhibitor (*b*).

to 0.12 mol g^{-1} h^{-1}. However, at *K* above 0.12 mol g^{-1} h^{-1} it approaches a constant value.

It seems important to consider the impact of the contact time on the rates of hydrogen uptake (V_H), nitro compound consumption (V_a), amine compound production (V_d), and chloride ion production ($w[Cl^-]$) (Figs 4 and 5).

In the presence of inhibitor, the rate of 3,4-DCNB consumption (V_a) (see Fig. 4) at high contact time decreases nearly two-fold, whereas the rate of hydrogen uptake (V_h) shows *ca.* a 1.8-fold decrease.

Correlation between the rate of 3,4-DCA formation (V_d) and *K* parameter (see Fig. 4) both in the presence and absence of pyridine is described by a curve with a maximum. It is worth noting that in the presence of the inhibitor, V_d magnitude decreases about 1.6 times.

At *K* ranging from 0.0052 to 0.073 mol g^{-1} h^{-1}, the intermediate product (see Fig. 5) is accumulated faster in the presence of inhibitor. With at further increase in the contact time ($K > 0.073$ mol g^{-1} h^{-1}) the intermediate product is accumulated faster in the absence of pyridine,

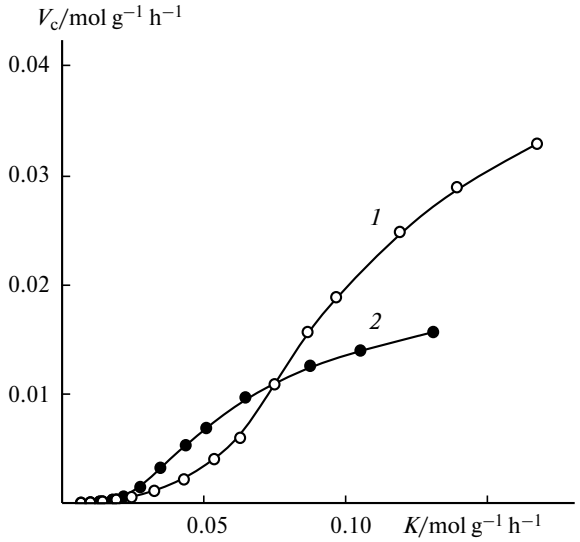


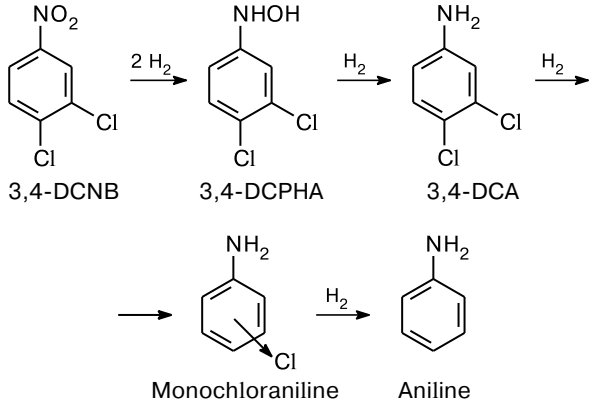
Fig. 5. Dependence of the accumulation rate of 3,4-DCPHA (V_c) on the contact time in the absence (*1*) and presence of the inhibitor (*2*).

although, as it follows from Fig. 2, the concentration of 3,4-DCPHA is lower in the presence of pyridine.

Without inhibitor, the rate of chloride ion elimination increases (see Fig. 4). When the contact time increases from a lowest value up to 0.094 mol g^{-1} h^{-1}, the rate of chloride ion formation ($w[Cl^-]$) increases, reaches a maximum and then decreases. One can assume that in the absence of the inhibitor the abstraction of chloride ion is not the only reaction proceeding at low contact times, and the side processes involving aniline can occur in the reaction system. In the presence of inhibitor, the accumulation rate of chloride ion gradually is reduced with increasing contact time.

Taking into account literature data and the results described above, catalytic hydrogenation of 3,4-DCNB in lower (C_1—C_4) aliphatic alcohols, which contain water, in the presence of Pt/C catalyst in neutral and acid media can be described by the following scheme.

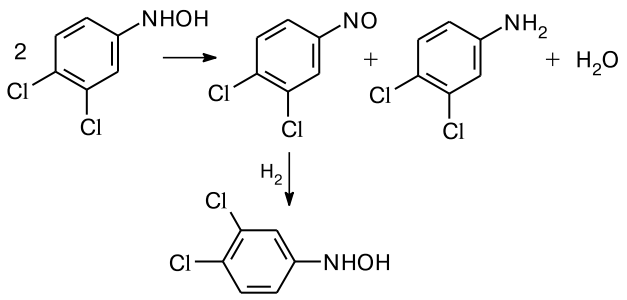
Scheme 1



The addition of the first hydrogen molecule to a nitro compound results in the formation of nitroso compound. However, in our experiments we failed to detect the compound in the reaction mixture, even in trace amounts. Obviously, under the applied conditions the nitroso compound is more reactive and can be adsorbed on the catalyst stronger than the initial nitro compound. That is why it can be considered as an acceptor of hydrogen. Accordingly, the starting nitro compound, 3,4-DCNB, converts into 3,4-DCPHA without desorption of nitroso compound into the reaction medium.

Generated 3,4-DCPHA can attach one hydrogen molecule and suffer transformation into the amine product through hydrogenation. It also can undergo disproportionation which is catalyzed by Pt/C and form amine product, nitroso compound, and water.[7] The obtained nitroso compound is hydrogenated to 3,4-DCPHA. Hence Scheme 1 of nitro compound transformation can be supplemented by Scheme 2.[8–9] The adequacy of this scheme is indirectly supported with the experimental data presented below.

Scheme 2



Under the conditions of hydrogenation, the generated RNO cannot be desorbed from the catalyst surface into the solution.

The amine product, 3,4-DCA, undergoes side dehalogenation with the chloride ion being abstracted just therefrom.[8]

Scheme 2 includes disproportionation of 3,4-DCPHA that was usually neglected in the earlier investigations of the kinetics of hydrogenation of aromatic nitro compounds. According to the Scheme 2, the reaction is independed of hydrogen pressure, so a definite amount of the amine product and nitroso compound is generated directly without involvement of hydrogen. Nevertheless, hydrogenation of the obtained nitro compound proceeds avoiding the step of desorption from the catalytic surface. This can give a favourable ground for the suggestion that conversion of nitro compound, if it follows the referred pathway, may depend on hydrogen pressure. Thus theoretically, 3,4-DCPHA can be formed via one-step hydrogenation of the starting RNO_2 and RNH_2 can be obtained through both hydrogenation of RNO_2 and disproportionation of 3,4-DCPHA without participation of hydrogen.

Earlier,[6] we showed that the kinetic constants of hydrogenation of a nitro compound can be determined by graphical linearization of the equation which describes the rate of consumption of this compound:

$$V_A = k_A f_H/[1 + b_c C/(b_a A) + b_d D/(b_a A)],$$

where V_A is the consumption rate of the nitro compound (mol g^{-1} h^{-1}); k_A is the rate constant of hydrogenation (mol g^{-1} h^{-1}); b_a, b_c, b_d, A, C, D are the adsorption coefficients and concentrations of 3,4-DCNB, 3,4-DCPHA, and 3,4-DCA, respectively; f_H is the efficiency factor for hydrogen. In the absence of pyridine the referred equation transforms into:

$$\left[\frac{k_A V_H^0}{V_A V_H} - 1\right] \cdot \frac{A}{C} = \frac{b_c}{b_a} + \frac{b_d D}{b_a C}, \quad (1)$$

In the presence of pyridine it can be written as

$$\left[\frac{k_A^* V_H^0}{V_A V_H} - 1\right] \cdot \frac{A}{C} = \frac{b_c^*}{b_a^*} + \frac{b_d^* D}{b_a^* C}, \quad (2)$$

where V_H is a current rate of hydrogen uptake; $V_H{}^0$ is the rate of hydrogen uptake in a regime where it is independent of the contact time; k_A and k^*_A are the rate constants of nitro compound consumption in the absence and presence of pyridine, correspondingly.

By processing the experimental data and using the Eqs (1) and (2), the relationships between b_d/b_a and b_d^*/b_a^*, b_c/b_a, and b_c^*/b_a^* can be determined as well as the ratio of b_c/b_d to b_c^*/b_d^* can be evaluated.

Figure 6 shows linearization of the Eqs (1) and (2) in the absence and presence of inhibitor, respectively. The obtained values of the constants are presented in Table 1.

As it follows from the data given in Table 1, admixture of pyridine in the reaction mixture makes adsorption of the amine product less preferable compared with adsorption of the nitro compound and *N*-arylhyrdoxylamine. As we showed earlier,[1] adsorptions of pyridine and 3,4-DCA are competitive and pyridine suppresses ad-

Table 1. The ratio of adsorption coefficients in Eqs (1) and (2)

Ratio of the adsorption coefficients	Conditions of hydrogenation	
	in the absence of pyridine	in the presence of pyridine
b_a/b_c	10.5	12.1
b_a/b_d	64.0	111.0
b_c/b_d	6.1	9.2

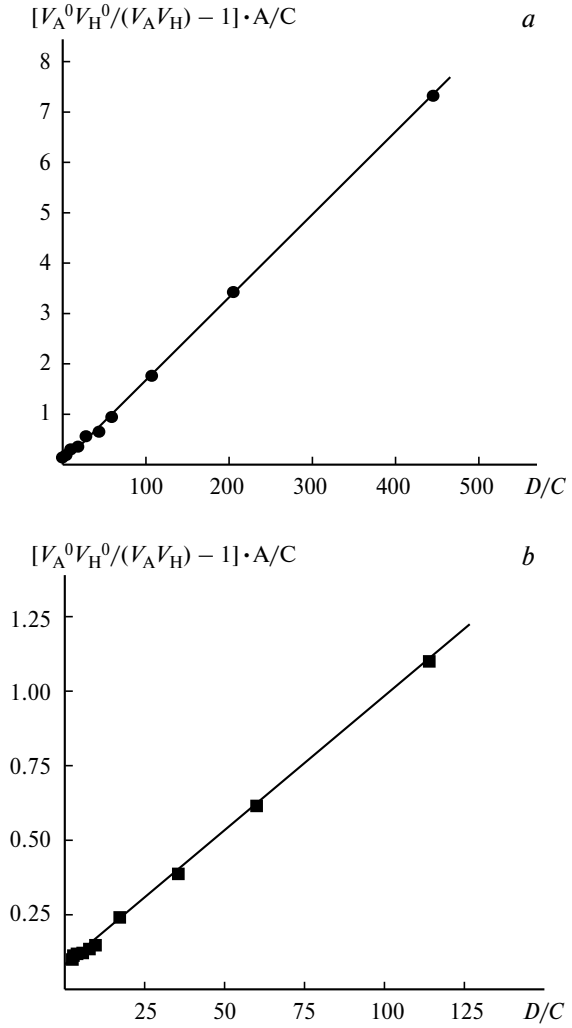


Fig. 6. Graphical analysis of Eqs (1) and (2) based on data of hydrogenation of 3,4-DCNB in the absence (*a*) and presence of pyridine (*b*).

sorption of the latter and decrease the rate of the following reactions. At the same time, pyridine non-competitively diminishes the rate of hydrogenation of nitro compound, while the rate of consumption of the intermediate product has a complicated pattern in the presence of pyridine.

An increase in the concentration of the intermediate product within low contact time interval in the presence of pyridine indicated above (see Fig. 2) can be explained by a weaker adsorption of the intermediate product compared to nitro compound. A decrease in the maximum concentration of the intermediate product in the presence of inhibitor may be related to an increased reaction rate of 3,4-DCPHA into the amine product caused by disproportionation proceeded in the presence of added pyridine.

In the range of low contact times (up to 0.05 mol g^{-1} h^{-1}), a decrease in the rate of hydrogenation of the intermediate product in the presence of pyridine, actually, is not compensated by corresponding decrease in the rate of consumption of the initial nitro compound. Hence in this range of the contact time the intermediate product concentration is higher in the presence of inhibitor. When the contact time is above 0.05 mol g^{-1} h^{-1}, the concentration of 3,4-DCPHA decreases faster in the presence of inhibitor. Such behavior is attributed to the predominate realization of the second scheme of the intermediate product consumption, the reaction rate of which markedly decreases in the presence of pyridine.

To sum up, hydrogenation of 3,4-DCNB over Pt/C catalyst both in the presence and absence of pyridine was studied under gradient-free flow conditions. It was shown that the inhibitor affects the conversion of the initial nitro compound to a much smaller extent than the reaction of dehalogenation.

An influence of inhibitor on the rate of accumulation and consumption of the intermediate 3,4-DCPHA was investigated. It was shown that a specific passway followed by the reaction of disproportionation plays a particular role in the pattern of conversion of the intermediate compound and it decreases its maximum concentration of this product in the reaction medium.

An influence of inhibitor on dehalogenation of the obtained chlorine derived amine product was investigated. It was established that introduction of pyridine inhibits side reactions such as chloride ion eliminating and suppresses a deeper conversion of aniline.

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