1412 *Russian Chemical Bulletin, International Edition, Vol. 67, No. 8, pp. 1412—1418, August, 2018*

Study of the products of platinum-catalyzed hydrogenation of chlorinated nitro and amino aromatic compounds at high degree of dehalogenation

V. G. Dorokhov,★ G. F. Dorokhova, and V. I. Savchenko

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (496) 522 3507. E-mail: vicd@icp.ac.ru

The kinetics of formation and consumption of the dehalogenation products during hydrogenation of 3,4-dichloronitrobenzene under static and gradient-free flow conditions and hydrogenation of *p*-chloroaniline under static conditions were studied in the presence of platinum supported on active carbon. In the former case, *p*-chloroaniline and aniline are the primary dehalogenation products; in the presence of the catalyst, they can react with each other giving biphenyl derivatives, whose synthesis and accumulation in the reaction mixture occur with a considerable delay and have not been investigated before.

Key words: liquid-phase hydrogenation, catalysis, aromatic nitro compounds, dehalogenation.

Liquid-phase hydrogenation of chlorinated aromatic nitro compounds in the presence of heterogeneous catalysts is used in industry to produce amino derivatives,[1] being the most efficient method for their synthesis. However, this catalytic hydrogenation process is complicated by the side elimination of chloride ions, which occurs to a higher or lower extent on all known hydrogenation catalysts. Together with chloride ion elimination from the obtained amino compounds, more extensive transformations of amines also take place and give additional side products.[2—5] Previously,[6—9] the kinetics of dehalogenation of the chloroanilines formed was investigated by measuring the initial rates of chloride ion accumulation, and the process was shown to be retarded by the reaction products and the solvent. No quantitative description of the stepwise elimination of chloride ions from chloroanilines containing more than one Cl in the molecule is available from the literature.

Most of the studies dealing with hydrogenation of halogenated nitro compounds are aimed at increasing the yield of halogenated amino compounds. Some recent studies in heterogeneous catalysis are directed towards the preparation of valuable products such as arylhydroxylamines,[10] which are formed as intermediates of reduction of substituted aromatic nitro compounds. A number of publications are devoted to hydrodechlorination of chloro amino compounds formed during hydrogenation.[10—14] In the published studies on hydrodechlorination, metals supported on new type materials, *e.g.*, nanocarbon materials or γ-Fe_2O_3 nanoparticles, have been recently used. The extents of halogen elimination, in particular, on contact with platinum, are, most often, moderate (not more than 3—5% and, only in rare cases, up to 10—12%). Under these conditions, the composition of hydrodechlorination products is quite predictable and virtually no other compounds are formed.

This study is devoted to catalytic hydrodechlorination of chloroanilines formed from the corresponding nitro derivatives on a platinum catalyst supported on active carbon, including identification of transformation steps of the starting reactants and intermediates formed at higher (more than 20—50%) degrees of chlorine elimination.

The present publication outlines the results of static experiments on catalytic hydrogenation of the amino compounds, 3,4-dichloroaniline (3,4-DCA) and *p*-chloroaniline (PCA), which are formed *in situ* upon 2.5%Pt/C-catalyzed hydrogenation of chlorinated nitro compounds (3,4-dichloronitrobenzene (3,4-DCNB) and *p*-chloronitrobenzene (PCNB)) at high (more than 20—50%) degrees of chlorine elimination. We expected that binuclear derivatives of chlorinated aromatic amines will be detected at these high degrees of chlorine elimination. However, static experiments consider two processes that are assumed to be independent of each other, namely, the initial hydrogenation of the nitro compound and the intermediate chlorinated *N*-arylhydroxylamine and the subsequent transformation of the resulting amino compound.[15] In a real process, especially in hydrogenation in stirred reactors, the above-indicated reactions occur simultaneously and affect each other. Therefore, hydrogenation of 3,4-DCNB and dehalogenation of 3,4-DCA were studied also under gradient-free flow conditions, in which hydrogenation of the nitro group and intermediates of its reduction proceed simultaneously with hydrodechlorination. Thus, it was possible to evaluate the influence of the starting nitro compound and intermediates on elimination of

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1412—1418, August, 2018.

chloride-ions from the amino derivative and its further conversion during the reaction

Experimental

3,4-Dichloroaniline (3,4-DCA) and *p*-chloroaniline (PCA) were obtained *in situ* during hydrogenation of 3,4-DCNB and PCNB conducted under static conditions in the presence of a platinum catalyst in a temperature-controlled catalytic "duck" (50±0.2 °C) in an aqueous solution of azeotropic 2-propanol. The samples from the reaction mixture were analyzed for the nitro compound, nitroso derivative, amino derivative, and the intermediate arylhydroxylamine. Analysis was carried out by voltammetry using a three-electrode circuit. During hydrogenation, the amount of absorbed hydrogen was recorded. The procedure of liquid-phase hydrogenation under static conditions has been described previously.[5] After hydrogen absorption (3 moles per mole of the starting nitro compound), the reaction mixture was a solution of either 3,4-DCA or PCA. This mixture was used to study hydrodechlorination of the chloro amino compound formed. The content of chloride ions was determined by potentiometric mercurometric titration. The contents of dehalogenation products and side products were determined by chromatography on a Khrom-4 instrument (FID, a 2.5 m×3 mm glass column, 15% polyethylene glycol adipate on chromaton DMCS, He as a carrier gas, ~140 °C). The samples were also analyzed on a Clarus 500 GC/MS instrument (Perkin-Elmer). A 30 m capillary column with 0.53 mm film thickness and with PE-5MS nonpolar stationary phase (5% biphenyl, 95% methylpolysiloxane) was used; the temperature was 220 °C; helium served as a carrier gas.

The procedure of liquid-phase catalytic hydrogenation under gradient-free flow conditions was reported previously.[15]

Commercial nitro compounds (analytical grade) were distilled twice and recrystallized twice (after purification, the content of the major substance was 99.7—99.9%) from isopropyl alcohol (chemically pure grade, TU-6-09402-75) of a nearly azeotropic composition. The Pt/C catalyst (BPL-2,5, TU-602-7-99-78) contained 2.2±0.2% platinum. The catalyst particle size was 80—200 μm. The catalyst loading was 0.3—1.0 g, the solution volume in the duck was 30—55 mL. Hydrogen (GOST 3022-80, grade A) with a hydrogen content of at least 99.99% based on dry gas was used as a reducing agent.

Results and Discussion

The results of stepwise 3,4-DCA hydrogenation experiments carried out under static conditions at 50±0.2 °C in the presence of the 2.5%Pt/C catalyst, which include data on 3,4-DCA consumption and the curves of accumulation of hydrogenation products with time, are shown in Fig. 1. The 3,4-DCA hydrogenation is accompanied by the formation and consumption of PCA (curve *2*) and aniline (*3*) and accumulation of the side products formed (*4*). For conversion times less than ~125 min, PCA and aniline are the major reaction products (the difference between the substrate concentration and the total concentration of the products does not exceed ~2%). After ~125 min, the concentrations of the intermediate PCA and aniline products reach the maximum values almost synchronously and then slightly decrease. After that, the formation of dehalogenation side products is significantly enhanced. By this time, the hydrogen absorption rate (Fig. 2) markedly decreases (~1.7-fold).

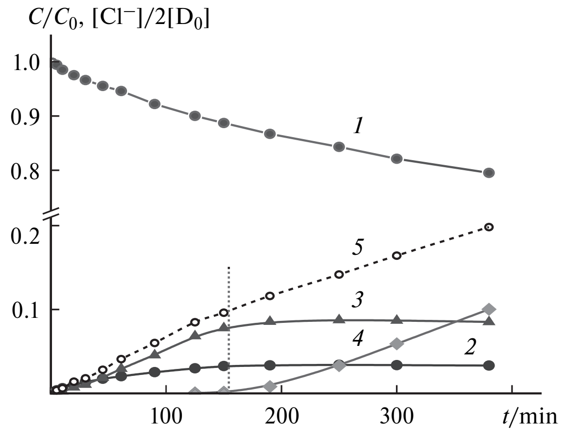


Fig. 1. Hydrogenation of 3,4-DCA in a solution of 2-propanol at 50±0.2 °C in the presence of the 2.5%Pt/C catalyst under static conditions: consumption of 3,4-DCA (*1*); formation of *p*-chloroaniline (*2*), aniline (*3*), and side products (*4*); accumulation of chloride ions ($[Cl^-]/2[D_0]$) (*5*), $[D_0]$ is the initial concentration of 3,4-DCA.

According to gas chromatography—mass spectrometry data, 4-aminobiphenyl is the major dehalogenation side product. MS (EI, 70 eV), m/z (I_{rel} (%)): 169 $[M^+]$ (34).

A minor amount of either 4-cyclohexylaniline or 4-phenylcyclohexylamine (up to ~2—3% relative to the amount of 4-aminobiphenyl) is also formed. With increasing conversion during further hydrogenation, the concentration of 3,4-DCA decreases very slowly.

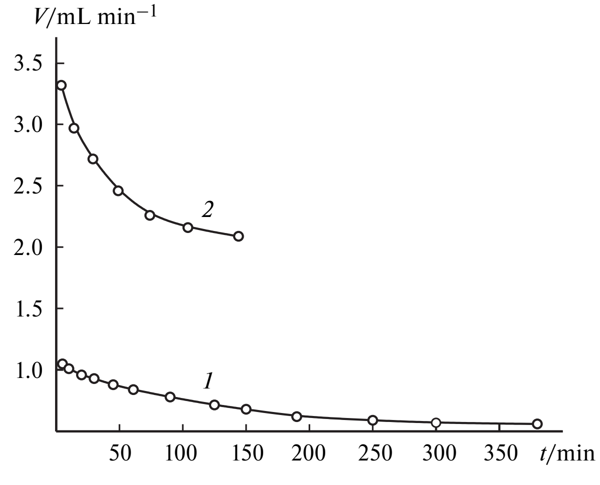


Fig. 2. Variation of the H_2 absorption rate *vs*. time during hydrogenation of 3,4-DCA (*1*) and PCA (*2*) under static conditions.

Similar trends in the product distribution are observed during PCA hydrogenation under static conditions. Figure 3 shows the curves of PCA consumption (*1*) and accumulation of aniline (*3*), side products (*4*), and chloride ions (*2*). The simultaneous variation of the hydrogen absorption rate during the reaction is shown in Fig. 2. The curve of accumulation of chloride ions up to the reaction time of ~50—52 min (the PCA conversion is ~20%) coincides almost exactly with the aniline accumulation curve. After ~75—77 min, when the degree of PCA conversion exceeds 30—32%, side products are found in the solution, namely, 4-aminobiphenyl and a minor amount (up to ~2%) of either 4-cyclohexylaniline or 4-phenylcyclohexylamine. 4-Aminobiphenyl is also formed after a time delay (see Fig. 3). The content of chloride ions corresponds to the overall accumulation of all dehalogenation products. The rate of H_2 absorption decreases almost 1.5-fold by the time the side reactions become noticeable (~75—80 min) (see Fig. 2). Previously,[10] only aniline and cyclohexylamine were detected in approximately equal amounts at PCA conversions of up to ~14%, with platinum supported on a nanocarbon composite being used as the catalyst in ethyl acetate or ethanol solvent.

It is known[16—18] that biphenyl and its derivatives can be formed upon catalytic dehalogenation of aryl halides with molecular hydrogen in an alkaline medium in the presence of a palladium catalyst. In our study, these products are formed with a platinum catalyst. Since this route of platinum-catalyzed dehalogenation of chloroanilines to give biphenyl derivatives is little studied, we will consider it in more detail.

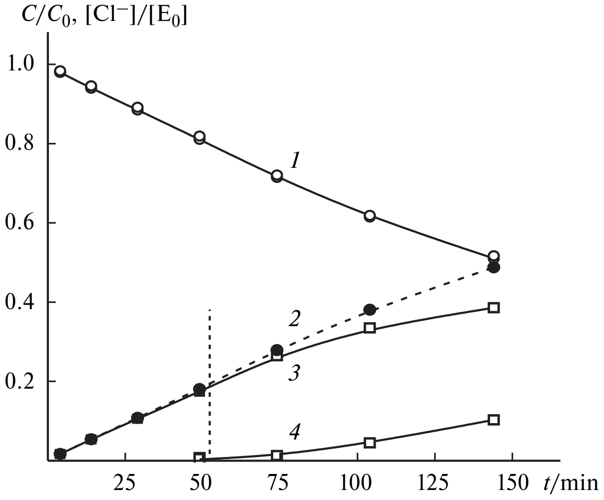
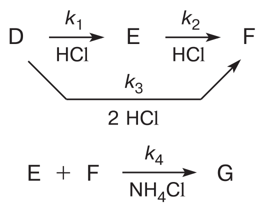


Fig. 3. Hydrogenation of PCA in 2-propanol at 50±0.2 °C in the presence of the 2.5%Pt/C catalyst under static conditions: (*1*) consumption of PCA, (*2*) accumulation of chloride ions ($[Cl^-]/[E_0]$, $[E_0]$ is the initial PCA concentration), (*3*) formation of aniline, (*4*) formation of side products.

The above experimental data obtained for a static process of 3,4-DCA hydrogenation suggest the following scheme for its dehalogenation and subsequent transformations of the products (Scheme 1).

Scheme 1



The following designations are used in Scheme 1: D is 3,4-DCA, E is PCA, F is aniline, G is 4-aminobiphenyl (as a sum with 4-cyclohexylaniline), and k_1—k_4 are the corresponding rate constants. Then the content of chloride ions during 3,4-DCA dehalogenation can be found using the equation

$$[Cl^-] = [E] + 2\,([F] + [G]). \qquad (1)$$

The applicability of Eq. (1) is confirmed by the plot for $[Cl^-]/[E]$ *versus* $([F] + [G])/[E]$, which is shown in Fig. 4. It can be seen that the data of static experiments and some data of dynamic experiments presented below fit satisfactorily in the straight line with expected parameters.

First, we will try to find out whether or not direct formation of aniline occurs in parallel during dehalogenation of 3,4-DCA. This question can be answered using the following approach. When the 3,4-DCA conversion is low, the E and F consumption for the formation of G can be ignored; in this case, using Scheme 1,[19] it is possible to derive the following approximate expressions for subsequent analysis:

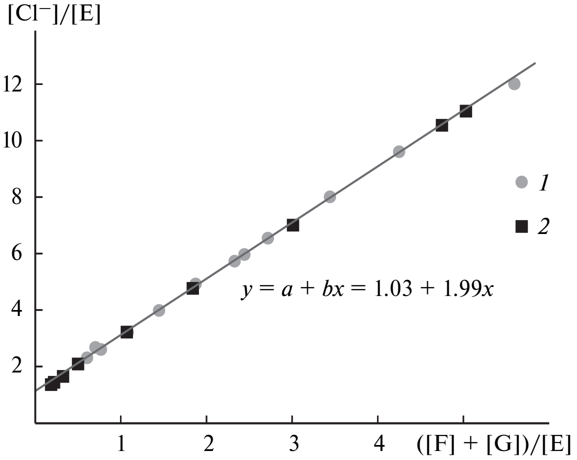


Fig. 4. Dependence of $[Cl^-]/[E]$ on $([F] + [G])/[E]$ under static (*1*) and gradient-free flow conditions (*2*).

$$[\mathrm{F}]/[\mathrm{E}] \approx k_3/k_1 + (k_2/k_1)(b_\mathrm{E}/b_\mathrm{D})([\mathrm{E}]/[\mathrm{D}]), \qquad (2)$$

$$\frac{[\mathrm{E}]}{\Delta[\mathrm{D}]} = \frac{k_1}{k_1 + k_3} - \frac{1}{2}\frac{k_2 k_1 b_\mathrm{E}}{(k_1 + k_3)^2 b_\mathrm{D}}\frac{\Delta[\mathrm{D}]}{[\mathrm{D}_0]} = b - a\frac{\Delta[\mathrm{D}]}{[\mathrm{D}_0]}, \qquad (3)$$

$$\frac{[\mathrm{F}]}{\Delta[\mathrm{D}]} = \frac{k_3}{k_1 + k_3} + \frac{1}{2}\frac{k_2 k_1 b_\mathrm{E}}{(k_1 + k_3)^2 b_\mathrm{D}}\frac{\Delta[\mathrm{D}]}{[\mathrm{D}_0]} = b_1 + a\frac{\Delta[\mathrm{D}]}{[\mathrm{D}_0]}, \qquad (4)$$

where k_1 and k_3 are the rate constants for the 3,4-DCA consumption according to successive and parallel pathways, respectively; k_2 is the rate constant for PCA consumption; b_E, b_D are the adsorption constants of PCA and 3,4-DCA, respectively (as shown previously,[4—6] the $b_\mathrm{E}/b_\mathrm{D}$ ratio is close to unity), $[\mathrm{D}_0]$ is the initial concentration of 3,4-DCA, and $\Delta[\mathrm{D}]$ is the consumption of D (moles).

If F is formed only from E, then $a = 0$; if F is formed only from D, then $b_1 = b = 0$. Provided that $a \neq 0$ and $b \neq 0$, F is formed in both successive and parallel pathways. Figure 5, *a—c* shows the graphical processing of Eqs (2)—(4), respectively. The difference between expressions (3) and (4) is plotted in Fig. 5, *d*. As can be seen from Fig. 5, the equations are properly linearized, and aniline formation during 3,4-DCA dehalogenation proceeds by both successive (from PCA) and parallel (from the starting dichloroaniline) pathways, with the successive pathway being more intense. This is an additional piece of evidence supporting the proposed scheme of transformations (see Scheme 1).

On the basis of the presented graphical data, it is possible to roughly estimate the ratio of the rate constants for the parallel and successive pathways of 3,4-DCA consumption: $k_3/k_1 \approx 0.24$.

The ratio of the products of kinetic and adsorption constants for dehalogenation of 3,4-DCA and PCA and aniline can also be estimated by assuming that the formation and consumption of PCA and aniline occur in a nearly quasi-steady-state mode (see Fig. 1). Indeed, starting from the time period of ~200 min, the concentrations of PCA and aniline become nearly constant, and approximate differential equations for the mass balance can be written as follows:

$$d[\mathrm{E}]/dt = k_1\theta_\mathrm{D} - k_2\theta_\mathrm{E} - k_4\theta_\mathrm{E}\theta_\mathrm{F} = 0,$$

$$d[\mathrm{F}]/dt = k_3\theta_\mathrm{D} + k_2\theta_\mathrm{E} - k_4\theta_\mathrm{E}\theta_\mathrm{F} = 0, \qquad (5)$$

where k_1—k_4 are kinetic constants (see Scheme 1); θ_D, θ_E, and θ_F are surface coverages by 3,4-DCA, PCA, and aniline, respectively, under the quasi-steady-state conditions. Solution of Eq. (5) gives

$$\frac{k_2}{k_1}\frac{b_\mathrm{E}}{b_\mathrm{D}} = \frac{[\mathrm{D}_\mathrm{st}]}{[\mathrm{E}_\mathrm{st}]}\frac{k_1 - k_3}{2k_1}, \qquad (6)$$

$$\frac{k_4}{k_1}\frac{b_\mathrm{F}}{b_\mathrm{D}}\theta_F = \frac{k_1 + k_3}{2k_1}\frac{b_\mathrm{D}}{b_\mathrm{E}}\frac{[\mathrm{D}_\mathrm{st}]}{[\mathrm{E}_\mathrm{st}]}, \qquad (7)$$

$$\frac{k_4}{k_2}\frac{b_\mathrm{F}\theta_\mathrm{F}}{b_\mathrm{E}} = \frac{k_1 + k_3}{k_1 - k_3}, \qquad (8)$$

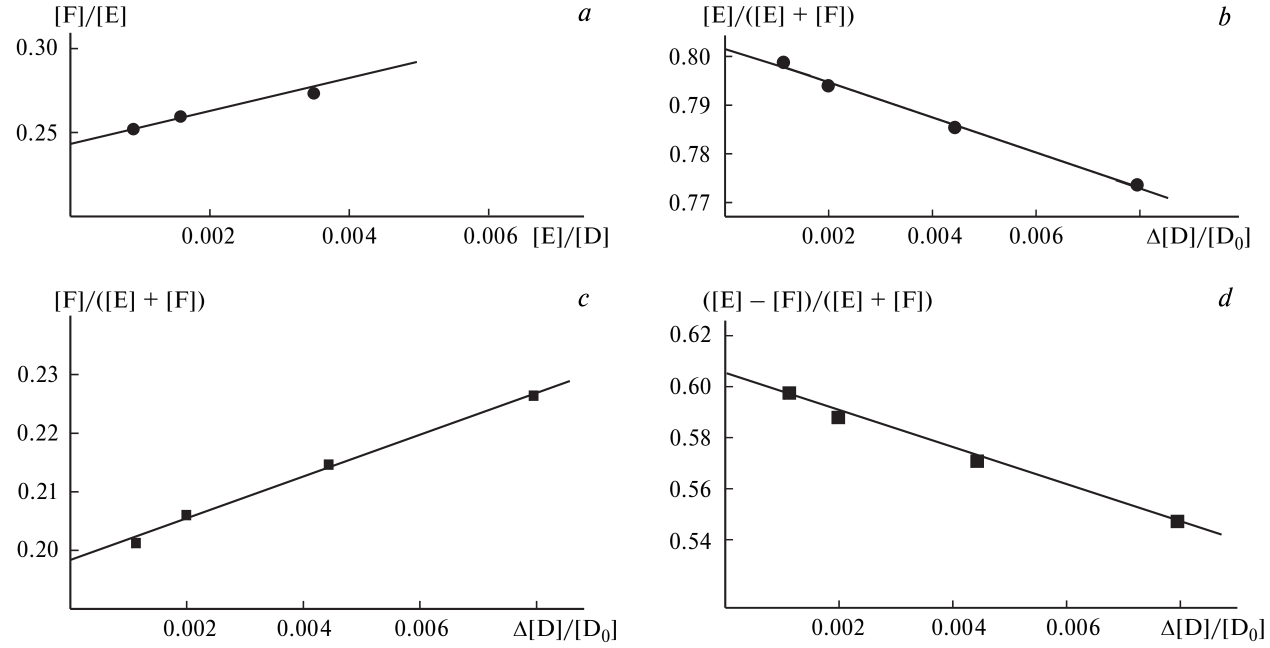


Fig. 5. Graphical analysis of Eqs (2)—(4) describing the initial segments of kinetic curves for dehalogenation of 3,4-DCA under static conditions: (*a*) Eq. (2), (*b*) Eq. (3), (*c*) Eq. 4, (*d*) difference between equations (3) and (4).

where $[D_{st}]$ and $[E_{st}]$ are the standard concentrations of 3,4-DCA and PCA, respectively.

By substituting the quasi-steady-state concentrations into Eqs (6)—(8), one can calculate the ratio of the products of the above-indicated kinetic constants by the adsorption constants

$(k_2/k_1)(b_E/b_D)$	9.14	$(k_4/k_1)(b_E/b_D)$	14.9
k_3/k_1	0.24	$(k_4/k_2)(b_F/b_E)\theta_F$	1.63
$(k_2/k_3)(b_E/b_D)$	38.1		

It is necessary to explain that some of the calculated ratios are represented as the quotient obtained by dividing the products of constants by adsorption coefficients. The latter are in the 1.1—2.0 range.[7—9]

Similar k_2/k_1 and k_4/k_1 ratios were also obtained for hydrogenation of PCA. Note that, as we demonstrated previously,[15] the dehalogenation of 3,4-DCA and PCA under static conditions proceeds in the kinetic region.

Consider the results of experiments on 3,4-DCA hydrogenation in the presence of the starting nitro compound, 3,4-DCNB, obtained under gradient-free flow conditions. Figure 6 depicts the distribution of product concentrations in the hydrogenation of 3,4-DCNB catalyzed by 2.5%Pt/C under gradient-free flow conditions as a function of contact load (*K* is the weight of the nitro compound (g) per h per g of the catalyst). It can be seen that with decreasing contact load, the concentration of the chloride ion in the solution increases, and the conversion of the nitro compound and consumption of the intermediate dichlorophenylhydroxylamine (3,4-DCPHA) simultaneously increase. Figure 7 shows experimental data on the distribution of dehalogenation products. It can be seen that at high (more than 12 g $(\mathrm{g\ h})^{-1}$) contact loads, only PCA and aniline are formed, while when the contact load is below 10 g $(\mathrm{g\ h})^{-1}$, the contents of aniline and 4-aminobiphenyl substantially increase, while building-up of PCA concentration slows down.

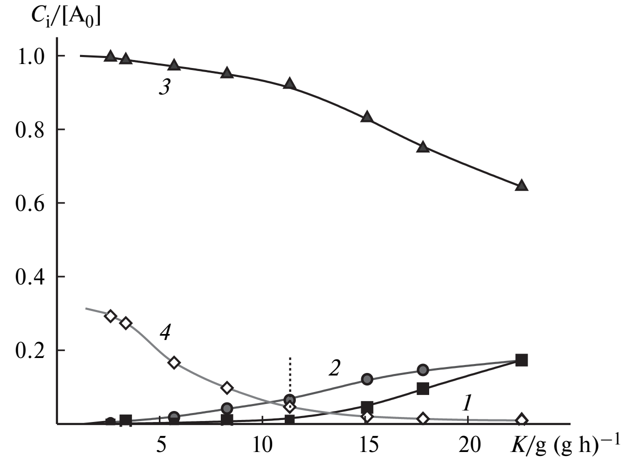


Fig. 6. Distribution of the relative concentrations ($C_i/[A_0]$) of the products of 3,4-DCNB hydrogenation in the presence of the 2.5%Pt/C catalyst under gradient-free flow conditions as a function of contact load (*K*): (*1*) 3,4-DCNB, (*2*) 3,4-DCPHA, (*3*) 3,4-DCA, (*4*) chloride ions. Here and in Figs 7 and 9, $[A_0]$ is the initial concentration of 3,4-DCNB.

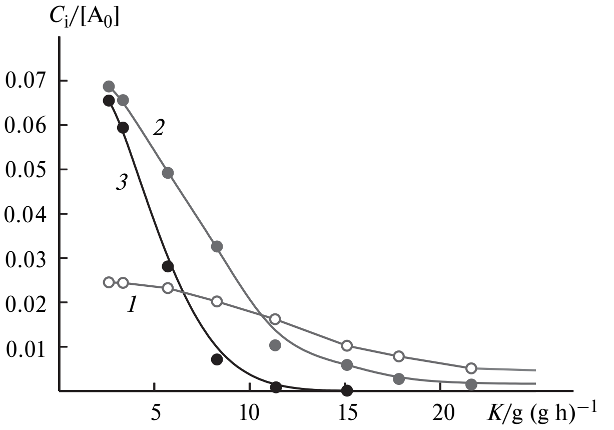


Fig. 7. Distribution of the dehalogenation products during hydrogenation of 3,4-DCNB in the presence of the 2.5%Pt/C catalyst under gradient-free flow conditions as a function of the contact load (*K*): (*1*) PCA, (*2*) aniline, (*3*) 4-aminodiphenyl.

Figure 8 presents the rates of consumption of 3,4-DCNB, formation of 3,4-DCA, and accumulation of chloride ions as functions of the contact load. It can be seen that the consumption rate of the nitro compound reaches a limiting value with increasing contact load; the rate of formation of the amino compound passes through a maximum, and also tends to a constant value. The accumulation rate of chloride ions increases with decreasing contact load, passes through a maximum, and then decreases.

The mass balance equations for dehalogenation process according to Scheme (1) proceeding during hydrogenation carried out under gradient-free flow conditions can be reduced to the following expressions:

$$k_1\theta_D f_H - k_2\theta_E f_H - k_4\theta_E\theta_F f_H - w[E_{st}] = 0,$$

$$k_3\theta_D f_H + k_2\theta_E f_H - k_4\theta_F\theta_E f_H - w[F_{st}] = 0,$$

$$k_4\theta_F\theta_E f_H - w[G_{st}] = 0, \qquad (9)$$

where k_1—k_4 are the reaction rate constants along the pathways of Scheme (1); w is the flow rate of the delivery of initial mixture ($\mathrm{L\ h}^{-1}$); $[E_{st}]$, $[F_{st}]$, and $[G_{st}]$ are PCA, aniline, and 4-aminobiphenyl concentrations, respectively; θ_E, θ_F are the surface coverages by PCA and aniline, respectively; f_H is the efficiency factor for hydrogen.

Using these relations, the following ratios of the constants were obtained for 3,4-DCNB hydrogenation experiments under gradient-free flow conditions: $k_3/k_1 = 0.14$, $k_2b_E/k_1b_D = 9.2$, $k_4b_E/k_1b_F = 23$.

Figure 9 shows the yields of 3,4-DCA upon the change in the contact load for the process under gradient-free flow

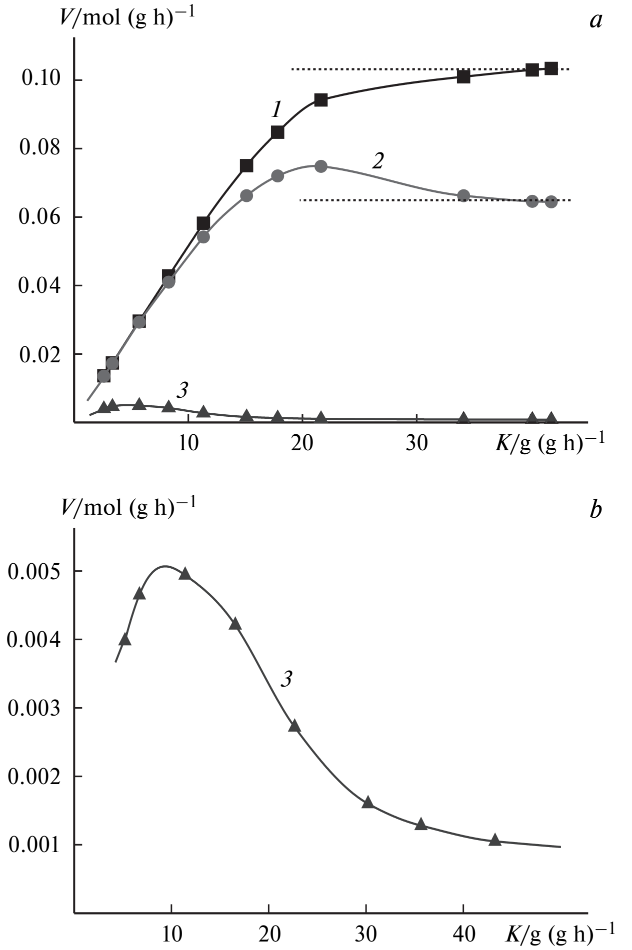


Fig. 8. Rates of 3,4-DCNB consumption (*1*), 3,4-DCA formation (*2*) and chloride-ion accumulation (*3*) *vs.* contact load during hydrogenation of 3,4-DCNB under gradient-free flow conditions (*a*). Initial region of the curve of chloride-ion accumulation (*b*).

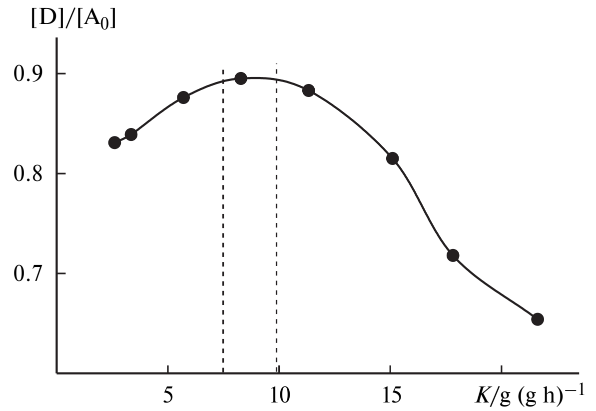


Fig. 9. Yield of 3,4-DCA *vs.* contact load during hydrogenation of 3,4-DCNB under gradient-free flow conditions.

conditions. It can be seen that the yield reaches a maximum when the contact load is in the range of 7.5—9.8 g (g h)$^{-1}$. When the contact load is more than 10 g (g h)$^{-1}$, the yield of the target amino compound decreases because of the presence of unreacted starting nitro compound and intermediate *N*-arylhydroxylamine derivative in the reaction mixture. When the contact load is less than 8 g (g h)$^{-1}$, the yield decreases due to dehalogenation side reactions. As can be seen, the highest yield of 3,4-DCA is about 90%; therefore, for the use of platinum catalysts in the hydrogenation of chlorinated aromatic compounds, it is necessary to additionally modify the catalysts, or modify the reaction medium by dechlorination inhibitors.[5]

Thus, it was shown that hydrogenation of 3,4-DCA in the presence of a platinum catalyst up to 12%—14% conversion of the starting 3,4-DCA gives PCA and aniline as the reaction products; when the conversions are more than 15%, the rate of elimination of chloride ions markedly decreases, the concentrations of the intermediate PCA and aniline are nearly constant, and 4-aminobiphenyl and minor amounts of 4-cyclohexylaniline appear in the dehalogenation product mixture. The hydrodechlorination of PCA also affords 4-aminobiphenyl. The kinetics of stepwise elimination of chloride ions from 3,4-DCA under static and gradient-free flow conditions was studied, and kinetic constants and their ratios were determined. The optimal conditions were identified, providing the highest yield of the chloro amino compounds and minimizing the formation of chloride ions in the catalytic hydrogenation of chloro nitro compounds.

The authors are grateful to E. I. Knerel′man and I. G. Shunina for conducting mass-spectrometric investigation of samples from the reaction mixtures.

The work was carried out as a part of Fundamental Research Program for the State Academies of Sciences for 2013—2020 (Project No. 0089-2014-0032).

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Received June 26, 2017;
in revised form April 25, 2018;
accepted June 9, 2018