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Kinetic Study of Liquid-Phase Hydrodechlorination of Hexachlorobenzene on Ni/C and 2%PdNi/C

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Abstract—Liquid-phase hydrodechlorination of hexachlorobenzene was kinetically studied in the presence of both nickel (Ni/C) and palladium-promoted nickel (2%PdNi/C) catalysts under different reaction conditions. Molecular hydrogen (at 1 and 20 atm) and sodium borohydride ($NaBH_4$) were used as reducing agents. In the presence of the nickel catalyst, the hydrodechlorination of C_6Cl_6 occurs via a consecutive mechanism (removal of one chlorine atom from the substrate at each stage), whereas with the 2%PdNi/C catalyst, the transformation of C_6Cl_6 occurs via both consecutive and multiplet mechanism (with the elimination of several chlorine atoms without desorption of the chloroaromatic substrate from the catalyst surface). The promotion of the nickel catalysts with palladium substantially changes the selectivity of formation of intermediate products of C_6Cl_6 dechlorination. The mechanism of hydrodechlorination of hexachlorobenzene was suggested that explained the presence of only certain products of partial dechlorination of hexachlorobenzene in the reaction medium.

INTRODUCTION

In recent years, because of increasing contamination of the environment, great attention has been given to the problems of practical application of processes for the removal of chlorine-containing organic compounds. In this respect, catalytic hydrodechlorination is of special interest. This process allows one not only to decompose organochlorine compounds, but also in many cases, to obtain useful products [1].

As shown by analysis of the published data, many works (e.g., [2]) have been devoted to catalytic hydrodechlorination over the last two decades. However, despite the progress achieved, many aspects of the mechanism of catalytic hydrodechlorination remain unclear. In addition, depending on the reaction conditions and catalysts, the mechanisms of dechlorination of organochlorine compounds can be different in particular cases [3–6].

We have previously shown that carbon-supported nickel and palladium compounds are efficient catalysts for hydrodechlorination of chloroaromatic compounds in ethanol-containing solvents under mild reaction conditions [7].

The purpose of this work is a kinetic study of the liquid-phase hydrodechlorination of hexachlorobenzene in the presence of both nickel and Pd-promoted nickel catalysts.

EXPERIMENTAL

Hexachlorobenzene (reagent grade) was used in experiments. Solvents, toluene (special purity grade) and 95% ethanol, were used after preliminary distillation. Sodium borohydride and transition metal chlorides of reagent grade were used.

Mono- and bimetallic catalysts were prepared as follows: calculated amounts of transition metal chlorides were dissolved in water and deposited onto a carbon carrier by evaporation. Next, the samples were reduced by an ethanol solution of $NaBH_4$ and washed three times with a water–ethanol mixture (ethanol : water = 1 : 1).

Nickel catalysts with a metal content of 1.7×10^{-4} (g-atom Ni)/(g Cat) (Ni/C) and promoted nickel catalysts with a total metal content of 1.7×10^{-4} (g-atom M)/(g Cat), where M = Ni + Pd, were used. The palladium-promoted nickel catalyst is designated as 2%PdNi/C, and the atomic percentage (2%) of the promoter (Pd) is equal to the ratio of the number of moles of palladium to the total number of moles of nickel and palladium (in percentage).

The carbon material known as Sibunit, which was described in detail in [8, 9], was used as the support. The Sibunit used in this work had the following parameters. Composition (wt %): carbon, 99.4; sulfur, 0.03; ash content, 0.2. The surface area with respect to argon was 350 m^2/g, and the average pore diameter was 7 nm.

Hydrodechlorination was carried out at a constant hydrogen pressure in a thermostatted glass reactor with a magnetic stirrer or in a thermostatted autoclave. In standard experiments, the freshly prepared catalyst containing 0.1 mmol metal was added to hexachlorobenzene (0.5 mmol) dissolved in a mixture (10 ml) of 95% ethanol and toluene or heptane (ethanol : toluene = 3 : 2). When $NaBH_4$ was used as the hydrogen source, $NaBH_4$ (6 mmol) dissolved in 95% ethanol was added

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Table 1. Degrees of dechlorination (x) of hexachlorobenzene in the presence of mono- and bimetallic catalysts

No.	Catalyst (Cat)	Ratio* S(C–Cl) : Cat : H	P_{H_2}, atm	T, °C	Time, h	x
1	Ni/C	30 : 1 : –	1	70	13	0.24
2	2%PdNi/C	30 : 1 : –	1	70	6.5	0.42
3	Ni/C	30 : 1 : –	20	50	7	0.25
4	2%PdNi/C	30 : 1 : –	20	50	5	0.89
5**	Ni/C	30 : 1 : 60	–	20	6	0.22
6**	2%PdNi/C	30 : 1 : 60	–	20	5.5	0.58

* For determination of the substrate (S) to metal (Cat) ratio, the amount of the substrate was estimated by the C–Cl fragment.

** $NaBH_4$ was used as the reducing agent at the atmospheric pressure of argon.

in portions to the reaction mixture. The ethanol solution contained an excess of NaOH necessary for binding the HCl evolved during the reaction. The mixture was intensely stirred (700 rpm). Samples for GLC analysis were taken from the reaction mixture during the reaction. Undecane was used as the internal standard.

Qualitative and quantitative analyses of the reaction products were carried out on an LKhM-80 chromatograph (a 2 m × 3-mm stainless-steel column packed with 5% SE-30 on Chromaton N-AW-DMCS; a flame-ionization detector; argon as the carrier gas, 60 ml/min) and an LKB 2091 gas chromatograph–mass spectrometer (a glass capillary column, 40 m × 0.3 mm, with the stationary phase SE-30).

RESULTS AND DISCUSSION

The data on the degrees of dechlorination (x) of hexachlorobenzene in the presence of mono- and bimetallic catalysts are presented in Table 1. Both molecular hydrogen and $NaBH_4$ dissolved in 95% ethanol were used as hydrogen sources. The x parameter, which determines the degree of dechlorination, was calculated as follows:

$$x = 1 - \frac{\sum_{i=0}^{6} iC_i}{6C_0},$$

where C_i is the molar concentration of the substrate containing i chlorine atoms in the molecule, and C_0 is the initial concentration of hexachlorobenzene.

It follows from the data in Table 1 that the highest (in the experiments performed) degree of dechlorination of C_6Cl_6 was achieved in the presence of the palladium-promoted nickel catalyst (2%PdNi/C) at an elevated hydrogen pressure (20 atm). Note that the use of $NaBH_4$ as the hydrogen source resulted in higher x values than those obtained at the atmospheric pressure of hydrogen.

The GC–MS analysis showed that only the following eight main products of dechlorination were detected in all experiments with hexachlorobenzene: pentachlorobenzene, 1,2,4,5- and 1,2,3,4-tetrachlorobenzenes, 1,2,3- and 1,2,4-trichlorobenzenes, 1,2-dichlorobenzene, chlorobenzene, and benzene. 1,2,3,5-Tetrachlorobenzene, 1,3,5-trichlorobenzene, and 1,3- and 1,4-dichlorobenzenes were presented in the liquid phase as traces.

The presence of biphenyl, other products of reductive coupling, and products of the hydrogenation of the solvent or the aromatic ring was not detected during the whole study.

The distributions of the reaction products (molar fractions) as functions of the degree of dechlorination of hexachlorobenzene in the presence of the Ni/C and 2%PdNi/C at 70°C and atmospheric pressure, and at 20 atm of hydrogen are presented in Figs. 1 and 2, respectively.

A similar distribution of the products of dechlorination of C_6Cl_6 on Ni/C and 2% PdNi/C at 20°C in the presence of sodium borohydride as the reducing agent is presented in Fig. 3.

The simplest reaction scheme that is consistent with the experimentally observed distributions of products may be the following (Scheme 1).

In Scheme 1, the addition of one H_2 molecule followed by the removal of HCl is implied at each stage of hydrodechlorination. However, this reaction mechanism does not completely agree with the data obtained in experiments using the 2%PdNi/C catalyst, because Figs. 1b, 2b, and 3b exhibit slopes that differed from zero for the curves corresponding to the formation of tetrachlorobenzene and trichlorobenzene isomers, dichlorobenzene, chlorobenzene, and benzene at the initial stage of dechlorination. If these reaction products were formed only by successive stages of elimination of one chlorine atom, the initial slopes of the curves corresponding to the formation of these substrates should be zero. Therefore, the reaction scheme describing the liquid-phase hydrodechlorination of hexachlorobenzene using 2%PdNi/C should include stages with multiplet elimination of chlorine atoms, i.e., stages in which more than one chlorine atom is eliminated without desorption of the dechlorinated sub-

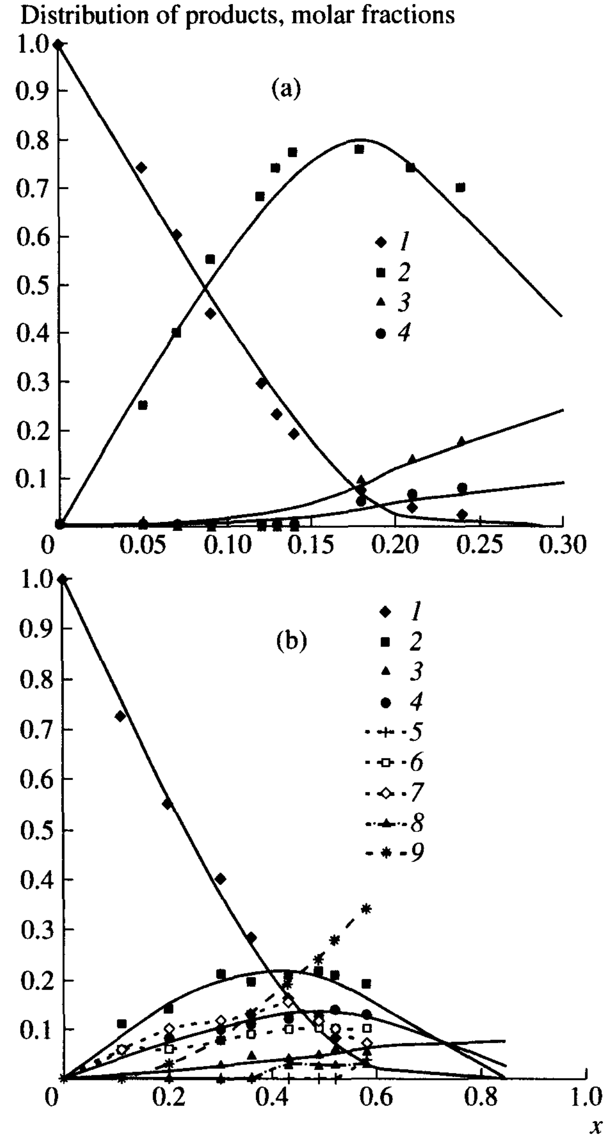


Fig. 1. Dependences of the distribution of the products of hydrodechlorination of C_6Cl_6 (molar fractions) on the degree of dechlorination (x) in the presence of (a) Ni/C and (b) 2%PdNi/C at atmospheric pressure of hydrogen and 70°C: (*1*) hexachlorobenzene; (*2*) pentachlorobenzene; (*3*) 1,2,4,5-tetrachlorobenzene; (*4*) 1,2,3,4-tetrachlorobenzene; (*5*) 1,2,4-trichlorobenzene; (*6*) 1,2,3-trichlorobenzene; (*7*) 1,2-dichlorobenzene; (*8*) chlorobenzene; and (*9*) benzene. Points indicate the experimental data, and curves represent the calculation by Scheme 3.

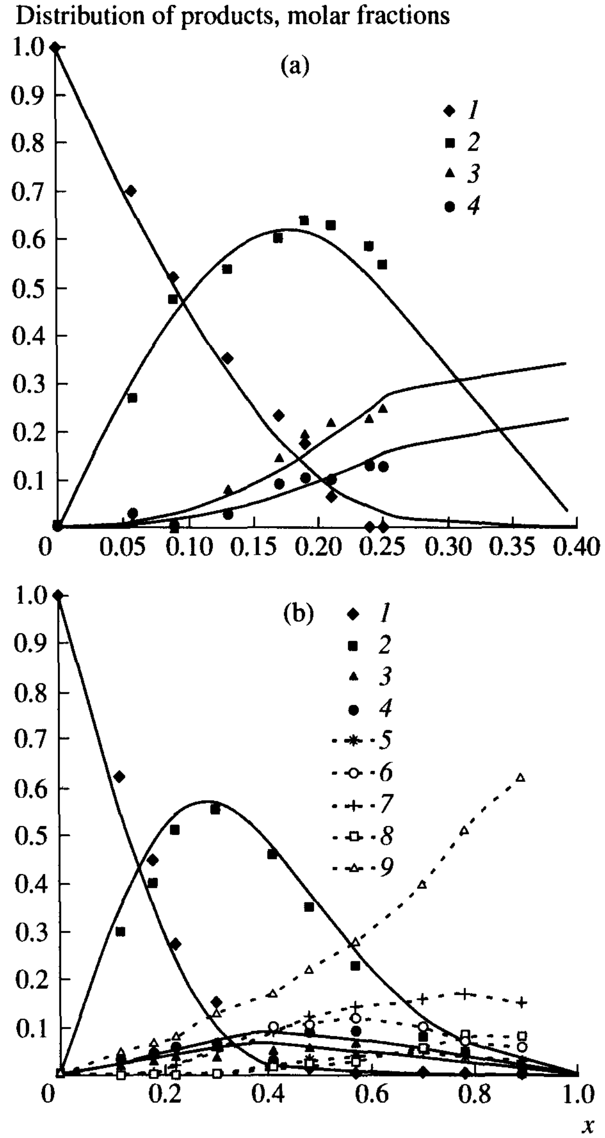


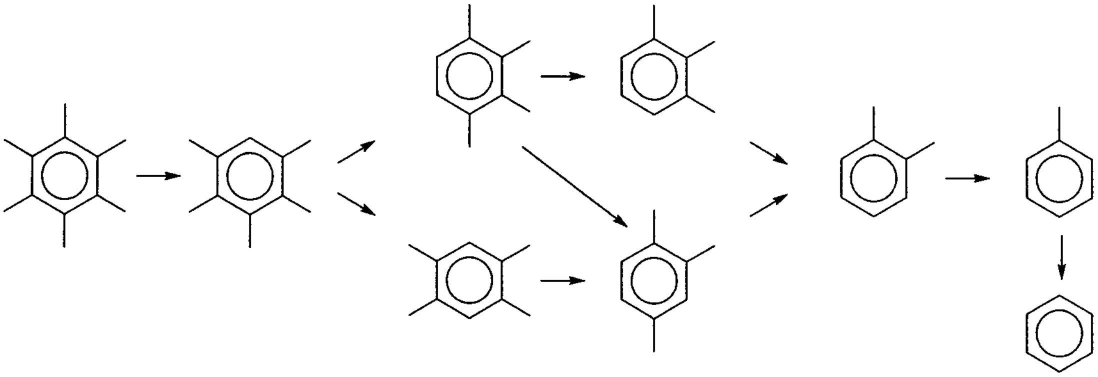
Fig. 2. Dependences of the distribution of the products of hydrodechlorination of C_6Cl_6 (molar fractions) on the degree of dechlorination (x) in the presence of (a) Ni/C and (b) 2%PdNi/C at 20 atm of hydrogen and 70°C: (*1*) hexachlorobenzene; (*2*) pentachlorobenzene; (*3*) 1,2,4,5-tetrachlorobenzene; (*4*) 1,2,3,4-tetrachlorobenzene; (*5*) 1,2,4-trichlorobenzene; (*6*) 1,2,3-trichlorobenzene; (*7*) 1,2-dichlorobenzene; (*8*) chlorobenzene; and (*9*) benzene. Points indicate the experimental data, and curves represent the calculation by Scheme 3.

strate from the catalyst surface. The complete scheme of the reaction for this case is presented below (Scheme 2).

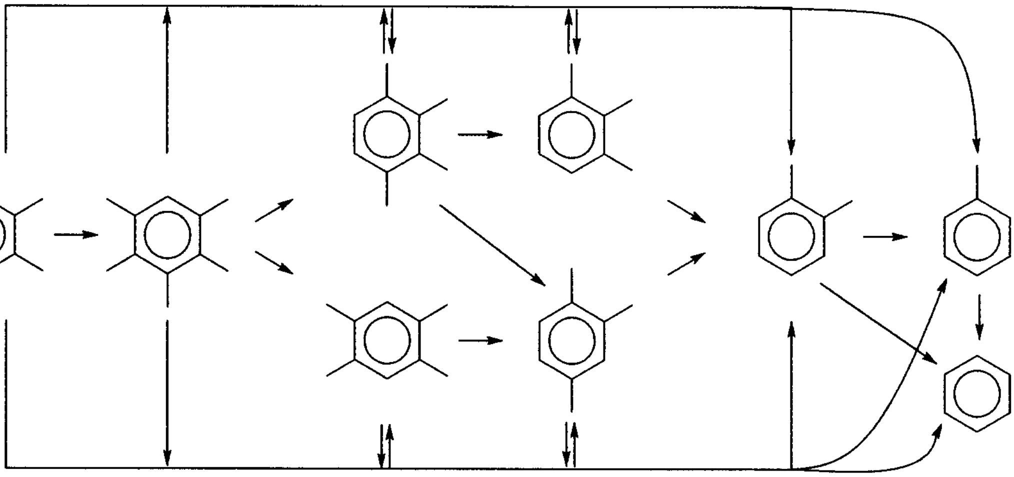
A variety of mechanisms for consecutive and multiplet dechlorination makes this scheme inappropriate for the estimation of the rate constants of all dechlorination routes. Therefore, we used a simplified scheme (Scheme 3) that describes only the initial part of this extended scheme, including hexachlorobenzene, pentachlorobenzene, and 1,2,3,4- and 1,2,4,5-tetrachlorobenzenes.

Here the stages of consecutive dechlorination accompanied by the desorption of intermediates are designated by solid arrows, and the stages including the multiplet removal of chlorine atoms are designated by dotted lines; k_{6-m} and k_{5-m} are the overall rate constants of dechlorination of C_6Cl_6 and C_6Cl_5H, respectively, via stages that are not included in Scheme 3.

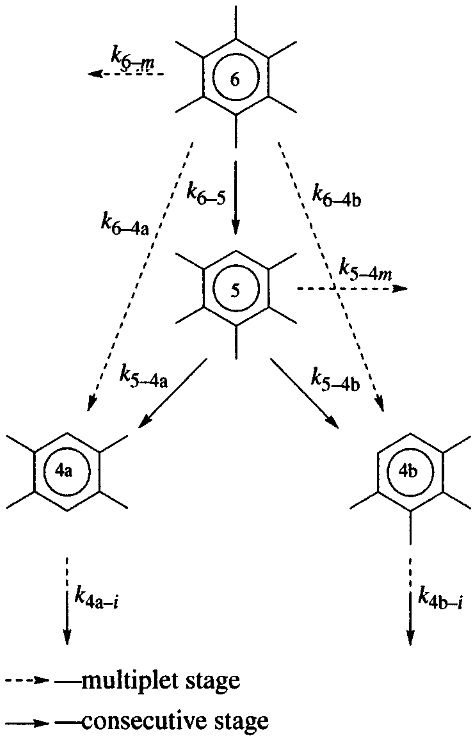
It has previously been shown for chlorobenzene that the hydrodechlorination reaction has a pseudo-first order with respect to the substrate under similar conditions. Therefore, it was assumed that the hydrodechlo-



Scheme 1.



Scheme 2.



Scheme 3.

rination rate of polychlorinated benzenes is also described by the pseudo-first-order equation with respect to the concentrations of these compounds.

It was also assumed that the type of the dependence of the reaction rate (r_{i-j}) used is a consequence of the description of the reaction system in terms of the Langmuir–Hinshelwood theory. The rate of each direct stage of hydrodechlorination $i \longrightarrow j$ is expressed as follows:

$$r_{i-j} = \frac{k'_{i-j}K_iK_{H_2}C_iP^n_{H_2}}{\left(1 + K_{H_2}P^n_{H_2} + \sum_i K_iC_i\right)^2},$$

where C_i is the concentration of the ith component of the reaction mixture, k'_{i-j} is the rate constant of the stage that describes the transformation of the ith species into the jth species, K_i is the equilibrium constant of adsorption for the ith species in this system (the equilibrium constants of adsorption of substrates that do not react at this stage are included in the formula), K_{H_2} is the equilibrium constant of hydrogen adsorption,

P_{H_2} is the partial pressure of hydrogen, and n is the reaction order with respect to H_2. Since all experiments were carried out at an unchanged pressure with a large excess of hydrogen, the $P^n_{H_2}$ term was included in the effective rate constant (k''_{i-j}), which is the product of k'_{i-j}, K_{H_2}, K_i, and $P^n_{H_2}$. Taking into account that the adsorption conditions are the same for all components of the reaction mixture, the term $(1 + K_{H_2}P^n_{H_2} + \sum K_iC_i)^2$ is reduced when the rate constants (r_{i-j}) are divided by each other.

The reaction route of hexachlorobenzene hydrodechlorination corresponding to Scheme 3 is described by a system of normalized differential first-order equations, where C_i is the concentration of the ith species in the liquid phase, and k_{i-j} is normalized k''_{i-j}, i.e., the normalized effective rate constant of the stage $i \longrightarrow j$:

$$k_{6\text{-}5} + k_{6\text{-}4a} + k_{6\text{-}4b} + k_{6\text{-}m} = 1,$$

$$\frac{dC_5}{dC_6} = \frac{k_{6\text{-}5}C_6 - (k_{5\text{-}4a} + k_{5\text{-}4b} + k_{5\text{-}m})C_5}{-(k_{6\text{-}5} + k_{6\text{-}4a} + k_{6\text{-}4b} + k_{6\text{-}m})C_6},$$

$$\frac{dC_{4a}}{dC_6} = \frac{k_{6\text{-}4a}C_6 + k_{5\text{-}4a}C_5 - k_{4a\text{-}i}C_{4a}}{-(k_{6\text{-}5} + k_{6\text{-}4a} + k_{6\text{-}4b} + k_{6\text{-}m})C_6},$$

$$\frac{dC_{4b}}{dC_6} = \frac{k_{6\text{-}4b}C_6 + k_{5\text{-}4b}C_5 - k_{4b\text{-}i}C_{4b}}{-(k_{6\text{-}5} + k_{6\text{-}4a} + k_{6\text{-}4b} + k_{6\text{-}m})C_6}.$$

This system was solved numerically by the fourth-order Runge–Kutta method.

The normalized effective rate constants k_{i-j} were selected in such a way that the mean-square deviations of the calculated data from the experimental values (R_i) were minimum. The R_i values were calculated by the equation

$$R_i = \frac{\left(\sum_{j=1}^{n_i}(C^{\text{exp}}_{i-j} - C^{\text{calc}}_{i-j})^2\right)^{1/2}}{n_i\frac{1}{2}\sum_{j=1}^{n_i}(C^{\text{exp}}_{i-j} + C^{\text{calc}}_{i-j})},$$

where C^{exp}_{i-j} and C^{calc}_{i-j} are the experimental and calculated amounts of the ith component converted into the jth component, and n_i is the number of experimental points for the ith component of the reaction medium. The unambiguous array of the k_{i-j} constants at which the best coincidence of the calculated and experimental data is achieved was determined by the successive minimization of all R_i. The accuracy of determination of k_{i-j} was 5–20%. These constants are summarized in Table 2.

Curves describing the transformations of hexachlorobenzene, pentachlorobenzene, and 1,2,4,5- and 1,2,3,4-tetrachlorobenzenes at a set of k_{i-j} constants corresponding to minimum R_i values are shown in Figs. 1–3 by solid lines; these curves were calculated by the above procedure.

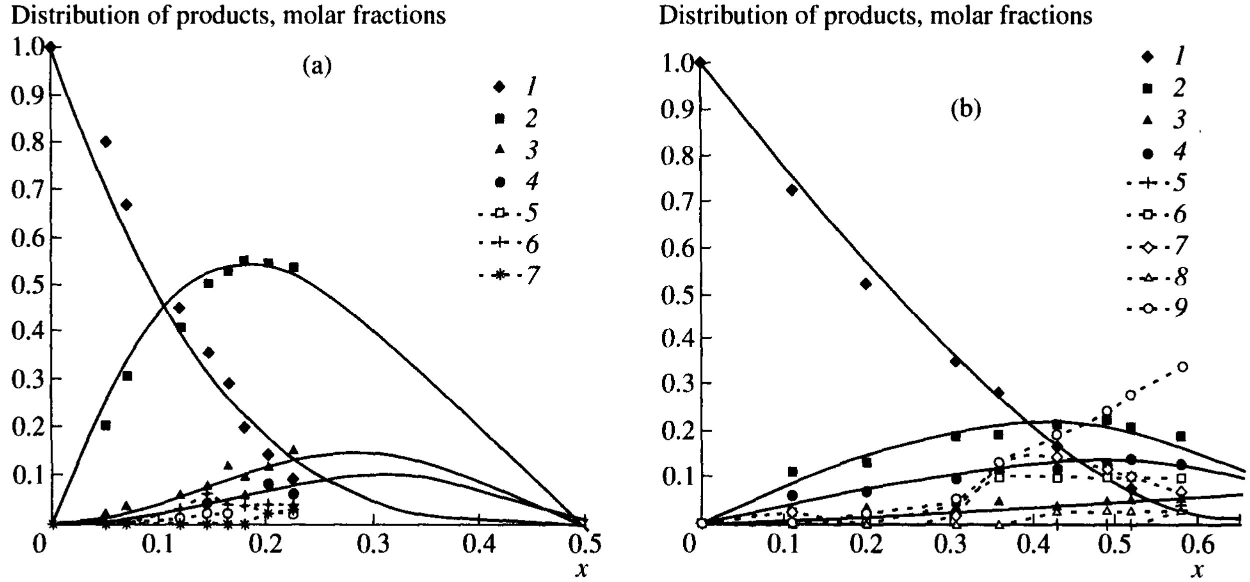


Fig. 3. Dependences of the distribution of the products of hydrodechlorination of C_6Cl_6 (molar fractions) on the degree of dechlorination (x) in the presence of (a) Ni/C–$NaBH_4$ and (b) 2%PdNi/C–$NaBH_4$ systems at 20°C in an inert atmosphere (Ar): (*1*) hexachlorobenzene; (*2*) pentachlorobenzene; (*3*) 1,2,4,5-tetrachlorobenzene; (*4*) 1,2,3,4-tetrachlorobenzene; (*5*) 1,2,4-trichlorobenzene; (*6*) 1,2,3-trichlorobenzene; (*7*) 1,2-dichlorobenzene; (*8*) chlorobenzene; and (*9*) benzene. Points indicate the experimental data, and curves represent the calculation by Scheme 3.

Table 2. Normalized effective rate constants ($k_{i\text{-}j}$) for hydrodechlorination of hexachlorobenzene

$k_{i\text{-}j}$	Ni/C, 1 atm H_2	2%PdNi/C, 1 atm H_2	Ni/C, 20 atm H_2	2%PdNi/C, 20 atm H_2	Ni/C, $NaBH_4$	2%PdNi/C, $NaBH_4$
$k_{6\text{-}5}$	1.0000	0.9091	1.0000	0.8261	1.0000	0.3714
$k_{6\text{-}4a}$	0	0	0	0.0435	0	0.0286
$k_{6\text{-}4b}$	0	0	0	0.0435	0	0.1714
$k_{6\text{-}m}$	0	0.0909	0	0.0869	0	0.4286
$k_{5\text{-}4a}$	0.0571	0.0545	0.1719	0.0435	0.3000	0.0571
$k_{5\text{-}4b}$	0.0245	0.5000	0.0937	0.0652	0.1000	0.1143
$k_{5\text{-}m}$	0	0.0909	0	0.0652	0	0.1429
$k_{4a\text{-}i}$	0.0735	0.0682	0.0938	0.3043	0.8125	0.0286
$k_{4b\text{-}i}$	0.0816	1.1360	0.0625	0.3043	0.4375	0.2857
$\frac{k_{6\text{-}4a} + k_{5\text{-}4a}}{k_{6\text{-}4b} + k_{5\text{-}4b}}$	2.3300	0.1090	1.8300	0.8000	3.0000	0.3700
Y	0	0.1240	0	0.2560	0	1.4210

Analysis of the normalized effective rate constants is also presented in Table 2.

The ratio of the sum of $k_{6\text{-}4a}$ and $k_{5\text{-}4a}$ to the sum of $k_{6\text{-}4b}$ and $k_{5\text{-}4b}$ is an indicator of the selectivity of formation of 1,2,3,4-tetrachlorobenzene depending on the catalyst nature and reaction conditions. The data in Table 2 show that 1,2,4,5-tetrachlorobenzene mainly forms at the stage of formation of tetrachlorobenzene isomers in the presence of the nickel catalyst, whereas 1,2,3,4-tetrachlorobenzene mainly forms in the presence of the 2%PdNi/C catalyst at both atmospheric pressure of hydrogen and P_{H_2} = 20 atm. The use of $NaBH_4$ as the source of hydrogen does not change this regularity.

The parameter *Y*, which is the ratio of the sum of the rate constants of stages with multiplet elimination of chlorine atoms to the sum of the rate constants of consecutive stages for hexa- and pentachlorobenzene, was calculated as follows:

$$Y = \frac{k_{6\text{-}4a} + k_{6\text{-}4b} + k_{6\text{-}m} + k_{5\text{-}m}}{k_{6\text{-}5} + k_{5\text{-}4a} + k_{5\text{-}4b}}.$$

It follows from the data in Table 2 that the promoter (Pd) increases the contribution of the multiplet stages to the hydrodechlorination of hexachlorobenzene as compared to the nonpromoted nickel catalyst (Ni/C), in the presence of which the process occurs almost completely via the consecutive route. When the pressure of hydrogen increases from atmospheric to 20 atm, the contribution of the multiplet stages approximately doubles in the presence of the promoted catalyst.

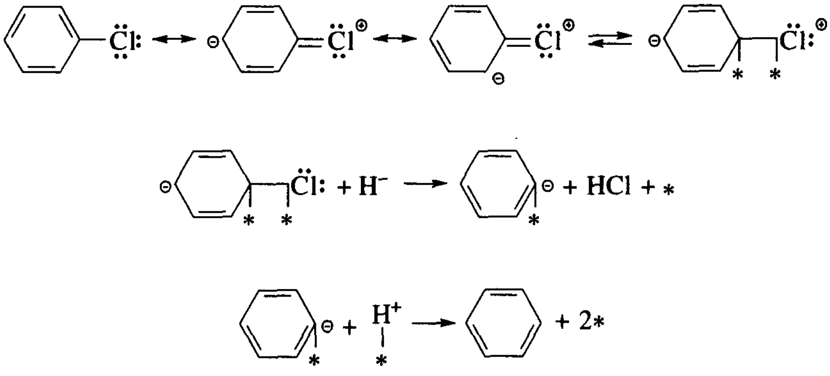
The data in Table 2 show that, when $NaBH_4$ is used as the hydrogen source, the hydrodechlorination in the presence of the 2%PdNi/C catalyst proceeds mainly via the multiplet route.

It is known that the C–Cl bond length in alkyl chlorides is 0.177 nm, and that in aryl chlorides is 0.169 nm due to the interaction of a lone electron pair of the chlorine atom with the π-cloud of the aromatic ring. Thus, the bond of chlorine with the aromatic ring has the character of a double bond [10]. Based on this fact, we suggest a reaction mechanism that explains our data and the results of other researchers.

As shown in [11], the catalytic hydrodechlorination of chlorobenzene is accelerated by electron-withdrawing substituents. This fact can be interpreted as the ability of electron-withdrawing groups to stabilize the C=Cl double bond due to the withdrawal of the electron density from the aromatic ring. Krans and Bazant [11] also showed that adsorption of chloroaromatic compounds is not dissociative. The presence of hydride species on VIII Group metals and protons formed during hydrogen adsorption was also assumed in [11].

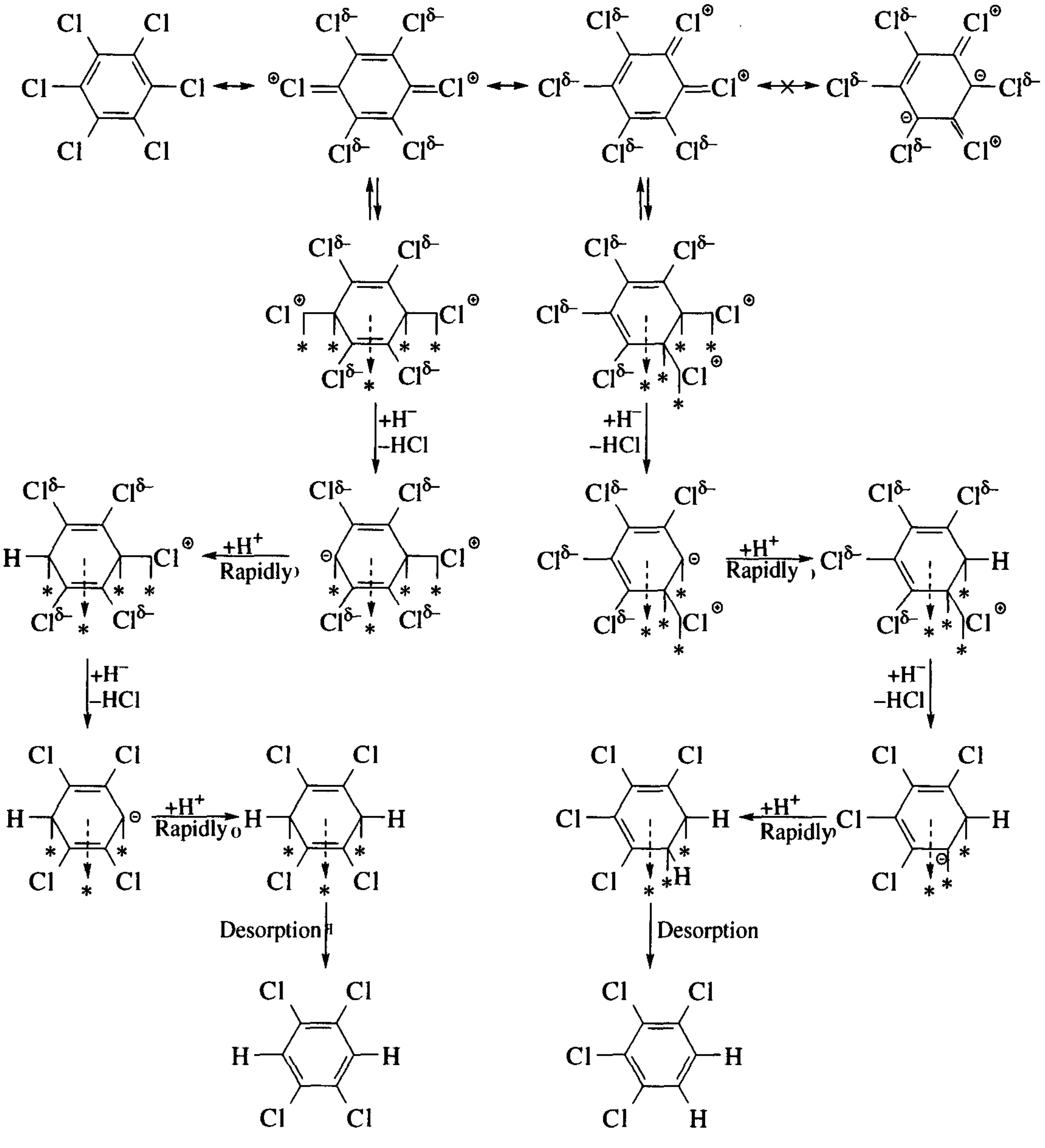
Based on similar considerations, La Pierre *et al.* [12] suggested a mechanism for hydrodechlorination of aryl chlorides (Scheme 4), according to which, at the first stage, adsorbed particles bound to two surface sites are attacked by a hydride ion to form an adsorbed phenyl anion, which is rapidly associated with a proton.

The chlorine atom is an electron acceptor in chloroaromatic compounds. Thus, the more chlorine atoms in the ring, the stronger the stabilization of the C=Cl bond. In addition, for multicentered adsorption of a polychloroaromatic compound on the catalyst surface, electrons of chlorine and the aromatic ring are partially withdrawn by *d*-orbitals of a transition metal (Pd, Ni), which also stabilizes the C=Cl bond. Therefore, two C=Cl bonds can be formed, and two chlorine atoms can be removed without desorption of the polychloroaromatic substrate from the catalyst surface after elimination of the first chlorine atom. This multiplet mechanism is presented in Scheme 5.

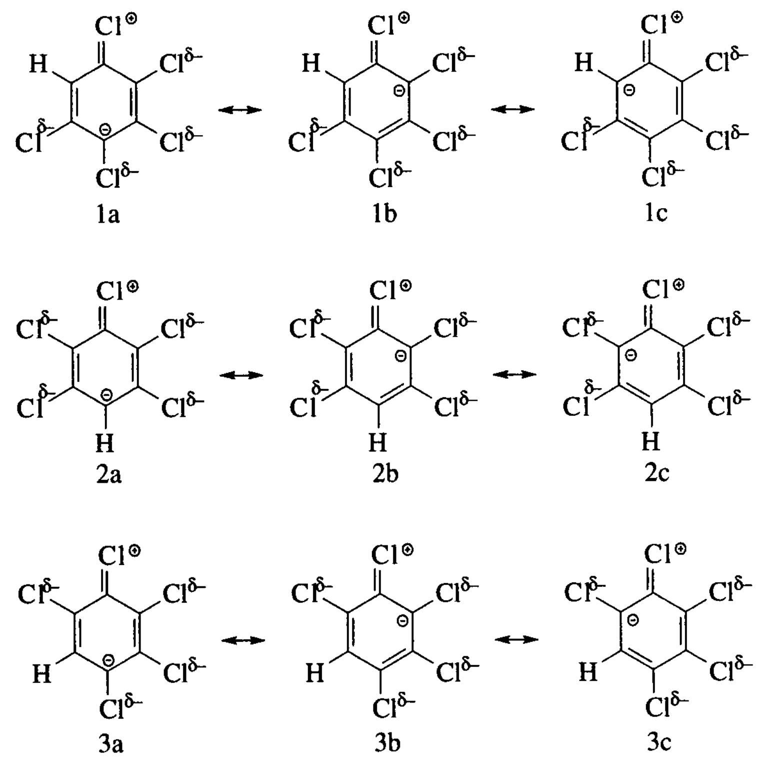


Adsorption sites at the catalyst surface are designated by asterisks

Scheme 4.



Scheme 5.



Scheme 6.

It can be assumed that adsorbed tetrachlorobenzene isomers formed from hexachlorobenzene can undergo further dechlorination without desorption from the catalyst surface.

Evidently, a mechanism of the consecutive removal of chlorine, which is similar to that described in [12], occurs in parallel to the multiplet mechanism. However, in this case, 1,2,3,5-tetrachlorobenzene was also not formed from pentachlorobenzene. For pentachlorobenzene, 1b and 2a species, in which the negative charge is located at the carbon atom attached to the hydrogen atom, are the most stable resonance structures that appear during the formation of the C=Cl bond in different positions relative to the hydrogen atom (Scheme 6). In all other structures, the negative charge is located at the carbon atom bound to the negatively charged chlorine atom. Thus, taking into account the Coulomb repulsion of like charges, we believe that the formation of 1,2,3,5-tetrachlorobenzene is improbable.

Similar consideration of the resonance structures of tetra- and trichlorobenzene isomers explains the absence of products of partial dechlorination of C_6Cl_6, such as 1,3,5-trichlorobenzene and 1,3-dichlorobenzene, in the reaction mixture.

Thus, the mechanism suggested for the transformation of hexachlorobenzene explains completely the experimentally observed composition of the products of partial dechlorination of hexachlorobenzene.

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