

# Kinetics and Mechanism of the Heterogeneous Catalytic Hydrogenolysis of Chlorobenzenes and Chlorocyclohexanes<sup>1</sup>

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**Abstract**—The catalytic hydrogenolysis of hexachlorobenzene and hexachlorocyclohexanes (isomer mixture) on a nickel–chromia catalyst and hexachlorobenzene hydrogenolysis intermediates (1,2,4,5-tetrachlorobenzene, 1,2,4-trichlorobenzene, 1,2-dichlorobenzene, and chlorobenzene) are studied. The hydrogenation of an aromatic ring does not occur in the presence of chemisorbed chlorine atoms on the catalyst surface. A reaction mechanism for chlorobenzene hydrogenation was proposed taking into account experimental evidence that, in the presence of chemisorbed chlorine on the catalyst surface, hydrogen in a dissociated state is firmly bound to the surface. It is found that the desorption of the resulting hydrogen chloride is the slowest step in chlorobenzene hydrogenolysis. The hydrogenolysis of hexachlorocyclohexanes occurs via a dehydrochlorination stage with the formation of trichlorobenzenes, which are subsequently converted into chlorobenzene and benzene.

## INTRODUCTION

The reactions of substituted benzenes with hydrogen can occur via the following two pathways: (a) hydrogen addition to the double bonds of a benzene ring with the formation of a hexane ring (hydrogenation) and (b) the abstraction of a substituent from the benzene ring followed by hydrogen atom addition (hydrogenolysis).

Many papers were devoted to the catalytic hydrogenation of benzene [1, 2], but the catalytic hydrogenolysis of halogenated benzenes is poorly studied as is evident from review [3].

The catalytic hydrogenolysis of chlorinated benzenes was primarily studied on metals supported on  $\gamma$ - $\text{Al}_2\text{O}_3$  or on sulfided nickel–molybdenum or cobalt–molybdenum samples supported on  $\gamma$ - $\text{Al}_2\text{O}_3$  [4–6]. Zhanaveskin *et al.* [3], who summarized published kinetic data, concluded that the hydrogenolysis of chlorinated benzenes occurs via the Langmuir–Hinshelwood mechanism. In this case, hydrogen and chlorobenzenes are adsorbed on the active sites of the same type. Moreau *et al.* [5, 6] suggested that hydrogenolysis occurs via the two-site adsorption of a molecule with the rupture of a C–X bond, where X is a halogen atom.

Therefore, the hydrogenolysis of chlorinated benzenes on a catalyst whose surface has two types of active sites, which chemisorb hydrogen and chlorinated benzene, respectively, is of interest. We chose the nickel–chromia catalyst, which consists of nickel and chromium oxide [7]. It was found [8] that hydrogen is dissociatively adsorbed on nickel. Halogen-atom trans-

fer from one molecule to another (transhalogenation) readily takes place on chromium oxide [9]. Taking into account the existence of two different active sites on the given catalyst, it was of interest to study the mechanism of hydrogenolysis on this catalyst and to compare experimental and published data.

## EXPERIMENTAL

Hexachlorobenzene and the following polychlorobenzene isomers that are intermediates in the hydrogenolysis of hexachlorobenzene were used as test materials in the reaction of catalytic hydrogenolysis: 1,2,4,5-tetrachlorobenzene (1,2,4,5-tetraCB), 1,2,4-trichlorobenzene (1,2,4-TCB), 1,2-dichlorobenzene (1,2-DCB), and chlorobenzene (CB). Hexachlorocyclohexanes were studied as an isomer mixture with the following composition (wt %):  $\alpha$ -hexachlorocyclohexane, 68;  $\beta$ -hexachlorocyclohexane, 6;  $\gamma$ -hexachlorocyclohexane, 12;  $\delta$ -hexachlorocyclohexane, 7;  $\epsilon$ -hexachlorocyclohexane, 5; and the balance heptachlorocyclohexane.

Experiments were performed on a nickel–chromia catalyst, which was prepared from nickel and chromium nitrate solutions according to a published procedure [7]. The chemical composition of the catalyst was as follows (wt %): nickel metal, 59.3; chromium oxide, 34.2; and a graphite binder, 6.5. The specific surface area of the catalyst before and after operation was equal to  $80 \pm 2$  m<sup>2</sup>/g. Before the experiments, the catalyst was heated in a hydrogen flow at 623 K for 10 h. According to data published in [7], the catalyst composition after this treatment corresponds to nickel supported on chromium oxide. Thereafter, the test catalyst sample (volume of 2 ml, particle size of 0.2–0.5 mm, and  $S_{sp} =$

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80 m<sup>2</sup>/g) was constantly kept in a hydrogen atmosphere during pauses between experiments.

Kinetic experiments were performed in a glass gradientless reactor designed by Korneichuk [10], and experiments on the simultaneous hydrogenation of chlorobenzene and benzene were performed in a glass flow reactor (with an inner diameter of 5 mm) with the same catalyst sample. The experiments were performed at 400–600 K; the contact time varied from 1 to 10 s.

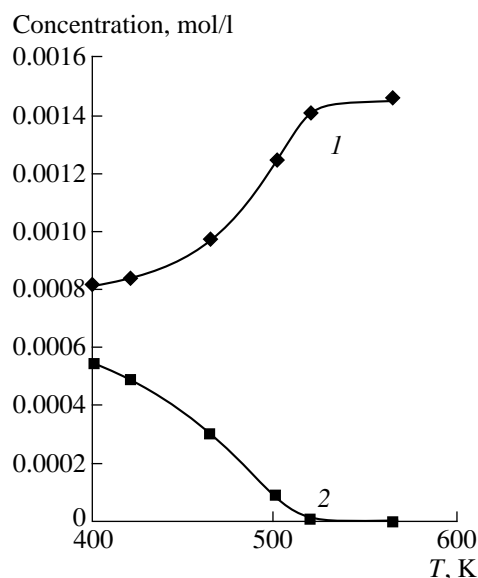
The reaction mixture was prepared by saturating a hydrogen or helium–hydrogen mixture with vapors of organochlorine compounds, which were placed in an evaporator at a certain temperature. The kinetic experiments were performed at hydrogen concentrations of 0.005–0.04 mol/l and organochlorine compound concentrations of  $1 \times 10^{-5}$ – $1.5 \times 10^{-3}$  mol/l. Because of the low partial pressure of hexachlorobenzene vapor, the experiments with this compound were performed in the concentration range  $1.0 \times 10^{-5}$ – $7.6 \times 10^{-5}$  mol/l.

The rates of reactions as functions of reactant concentrations were studied by maintaining a constant concentration of one of the reactants (hydrogen or an organochlorine compound). Note that, in the course of the hydrogenolysis of chlorobenzenes and chlorocyclohexanes, the catalyst operation was stable for more than 100 h without detectable changes in the activity. The initial substances and organic products were analyzed by chromatography using a flame-ionization detector. Samples for analyses were taken directly from gas flows at the inlet and outlet of the reactor using the same sampling valve, which was kept at 473 K.

## RESULTS AND DISCUSSION

Benzene and chlorobenzenes with fewer chlorine atoms than in the parent compound were the chlorobenzene hydrogenolysis products. The products of aromatic ring hydrogenation (cyclohexene, cyclohexadiene, and cyclohexane) were not formed. Similar data (the absence of cyclohexane in the hydrogenolysis of chlorobenzenes on nickel and palladium catalysts) have been published [11, 12]. Cyclohexane was detected in the products of hydrogenolysis on platinum catalysts [13, 14].

In the simultaneous hydrogenation of chlorobenzene and benzene, the amount of the latter increases with temperature (Fig. 1, curve 1) and the amount of chlorobenzene decreases to zero (curve 2). The calculated material balance with respect to carbon demonstrates that the amount of benzene at the reactor outlet increased and the concentration of chlorobenzene decreased by the same value (benzene was not hydrogenated). If the chlorobenzene supply to the reactor was stopped, cyclohexene and cyclohexane appeared in the reaction products after some time (~1 h). The activity of the catalyst in benzene hydrogenation was completely restored by heating at 573 K in a hydrogen flow. The recovery of the catalyst activity was judged



**Fig. 1.** Concentrations of (1) benzene and (2) chlorobenzene in the reaction mixture in their simultaneous hydrogenation on a nickel–chromia catalyst as functions of temperature (the benzene and chlorobenzene concentrations in hydrogen in the starting reaction mixture were  $8.18 \times 10^{-4}$  and  $5.48 \times 10^{-4}$  mol/l, respectively; the space velocity was 2400 h<sup>-1</sup>).

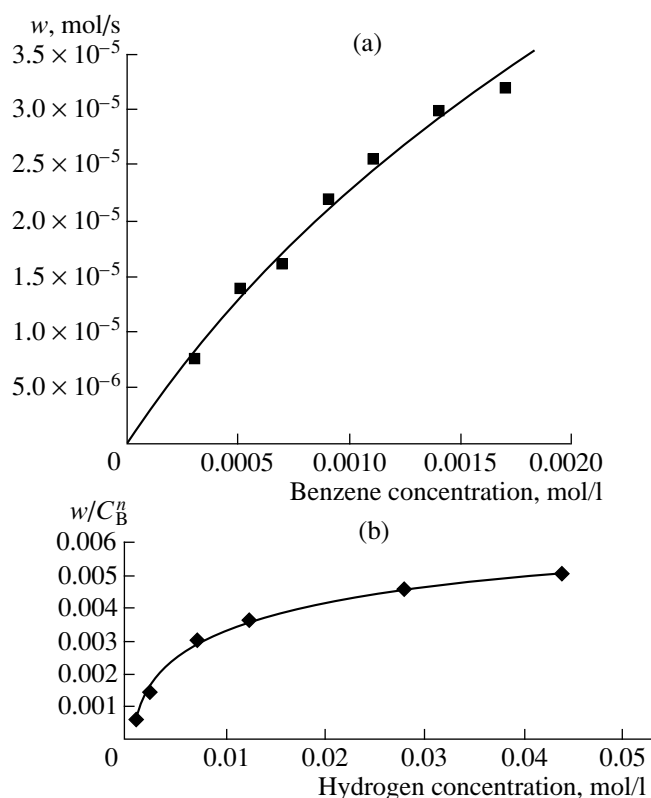
from the termination of hydrogen chloride release from the surface.

These data indicate that the hydrogenation of an aromatic ring does not take place in the presence of chemisorbed chlorine atoms or hydrogen chloride on the surface of a nickel–chromia catalyst.

Figure 2 demonstrates the rate of benzene hydrogenation as a function of benzene concentration in hydrogen and the effect of hydrogen concentration on the rate of this reaction.

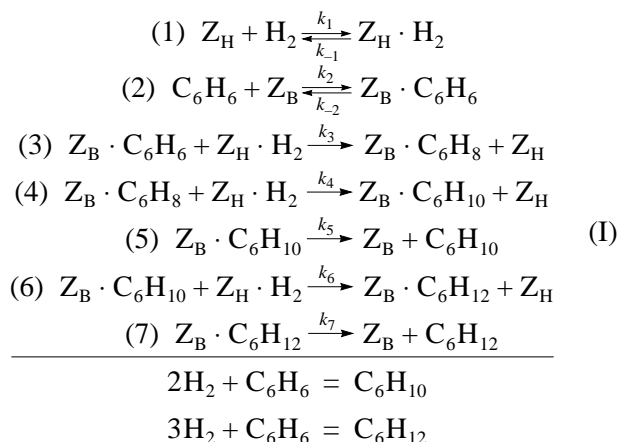
Cyclohexene and cyclohexane were the products of benzene hydrogenation, and cyclohexadiene was not detected. The reaction orders with respect to benzene and hydrogen are 0.6 and 0.4, respectively; these values are consistent with published data [15, 16] obtained on nickel-containing catalysts. The absence of maxima on the rate-vs-concentration curves may indicate that benzene and hydrogen are adsorbed on different catalyst sites [17]. In the test nickel–chromium catalyst, metallic nickel and chromium oxide can be assumed to be these two types of sites.

Gaidai *et al.* [18] found that the hydrogenation of benzene on a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst is performed by weakly bound molecular hydrogen, whereas isotope exchange takes place through firmly bound atomic hydrogen. Taking into account these data and our experimental



**Fig. 2.** Rate of benzene hydrogenation on a nickel-chromia catalyst at 700 K and a space velocity of  $2400 \text{ h}^{-1}$  as a function of (a) benzene concentration in hydrogen or (b) hydrogen concentration (at a constant initial benzene concentration of  $1.6 \times 10^{-3} \text{ mol/l}$ ).

results on the kinetics of benzene hydrogenation, we propose the following mechanism of this reaction:



In this reaction scheme, we suggest that undissociated hydrogen is adsorbed on the active sites  $\text{Z}_\text{H}$  (metallic nickel), whereas benzene and its hydrogenated forms are associated with the active sites  $\text{Z}_\text{B}$ ; we believe that the latter sites exist on the chromium oxide. Because cyclohexadiene was not detected in the reac-

tion products, this scheme does not involve its release into the gas phase.

As was found by thermodynamic calculations [19, 20], step (I.3) is a rate-limiting step. Thus, the rate law for benzene conversion ( $w_\text{B}$ ) as a function of reactant concentrations is

$$w_\text{B} = \frac{k_3 b_1 C_\text{H} b_2 C_\text{B}}{(1 + b_1 C_\text{H})(1 + b_2 C_\text{B})}. \quad (1)$$

In this equation,  $b_1 = k_1/k_{-1}$ ,  $b_2 = k_2/k_{-2}$ ;  $k_3$  is the rate constant of step (I.3);  $C_\text{H}$  and  $C_\text{B}$  are the concentrations of hydrogen and benzene, respectively.

The rate constants and equilibrium constants of reaction steps were optimized. For example, in the hydrogenation of benzene at 400 K, the following calculated values of constants best fitted the experimental data:  $b_1 = k_1/k_{-1} = 4.9 \times 10^{-8}$ ,  $b_2 = k_2/k_{-2} = 304$ , and  $k_3 = 45332$ .

The equilibrium constants of benzene (step (I.2)) and hydrogen (step (I.1)) adsorption suggest that, in the case of benzene, the equilibrium is shifted to the adsorption of a  $\text{C}_6\text{H}_6$  molecule on an active site, whereas the equilibrium with hydrogen, on the contrary, is shifted to the desorption from the catalyst surface.

It was found [9] that the transhalogenation reaction of halobenzenes is facile in the presence of  $\text{Cr}_2\text{O}_3$ . Halogen-atom transfer from one halobenzene molecule to another on the surface of a catalyst can occur only in the case of the dissociative adsorption of a molecule with the formation of a phenyl group and a halogen or hydrogen atom. We believe that the presence of chlorine atoms on the catalyst surface in our experiments and of sulfur atoms in experiments with sulfided catalysts [5, 6, 21] is favorable for the dissociative adsorption of hydrogen, which facilitates the reaction of hydrogenolysis.

We performed an experiment described below to study whether or not chlorobenzenes would react with chemisorbed hydrogen. Hydrogen was replaced with helium in the reaction mixture after 1,2,4,5-tetraCB hydrogenolysis at 483 K. It can be seen (Fig. 3) that, in spite of the absence of hydrogen from the gas phase, the reaction of 1,2,4,5-tetraCB hydrogenolysis took place for a long time. These data support the fact that the reaction of chlorobenzene hydrogenolysis involves hydrogen chemisorbed on the surface and in the bulk of the catalyst.

The results of the study of 1,2-DCB hydrogenolysis (Fig. 4) demonstrate that the selectivity to chlorobenzene decreased with temperature (curve 2), whereas the selectivity to benzene increased (curve 3). This indicates that the chlorobenzene formed in the reaction was converted into benzene.

As the temperature was increased in the hydrogenolysis of 1,2,4-TCB, the selectivities to 1,2-DCB and 1,4-DCB decreased, the selectivity to benzene con-

tinuously increased, and the selectivity to CB passed through a maximum (Fig. 5). This behavior suggests that 1,2-DCB, 1,4-DCB, and CB are intermediates in the hydrogenolysis of 1,2,4-TCB to benzene.

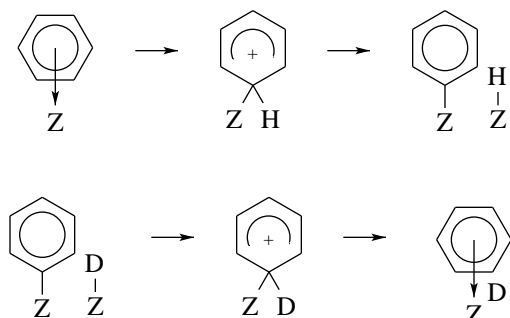
We found by varying the contact time ( $\tau$ ) of the reaction mixture containing hexachlorobenzene and hydrogen (Fig. 6) that the selectivities to pentachlorobenzene (PCB), 1,2,4,5-tetraCB, and 1,2,3,4-tetraCB decreased with  $\tau$ , the selectivities to 1,2,3-TCB, 1,2,4-TCB, and 1,2-DCB passed through a maximum, whereas the selectivities to CB and benzene continuously increased. Thus, it is evident that an increase in the contact time is favorable for the consecutive transformation of highly chlorinated benzenes to less chlorinated species.

The above data indicate that the hydrogenolysis of chlorinated benzenes occurs by a similar mechanism through the consecutive formation of less chlorinated benzenes.

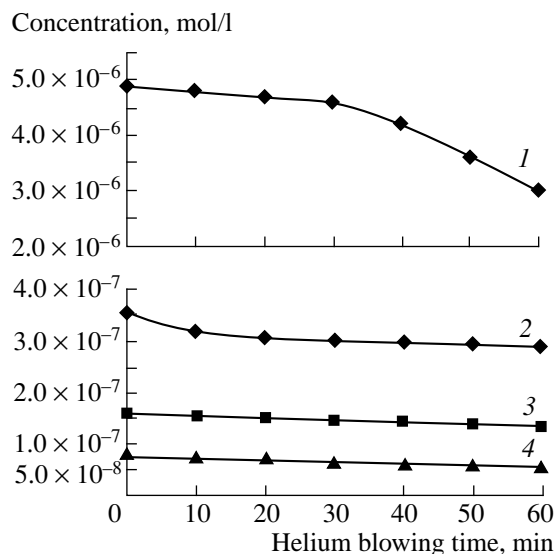
The similarity in reaction mechanisms for the hydrogenolysis of chlorobenzenes was also supported by the similarity in the reaction orders with respect to reactants and the activation energies of the reactions. The table summarizes data on the reaction orders with respect to initial compounds and hydrogen. The reaction orders with respect to hexachlorobenzene are somewhat different from the corresponding values for other chlorobenzenes because the experiments were performed at lower hexachlorobenzene concentrations in hydrogen; it is well known [33, 34] that this leads to an increase in the order of reaction.

It can be seen that the reaction orders with respect to the initial reactants for various chlorobenzenes are lower than unity. This fact indicates that hydrogenolysis takes place in a chemisorbed state. The reaction rates as functions of concentration exhibit no maxima for all of the chlorobenzenes examined in this work. This suggests the adsorption of chlorobenzene and hydrogen molecules on different active sites of a catalyst [17].

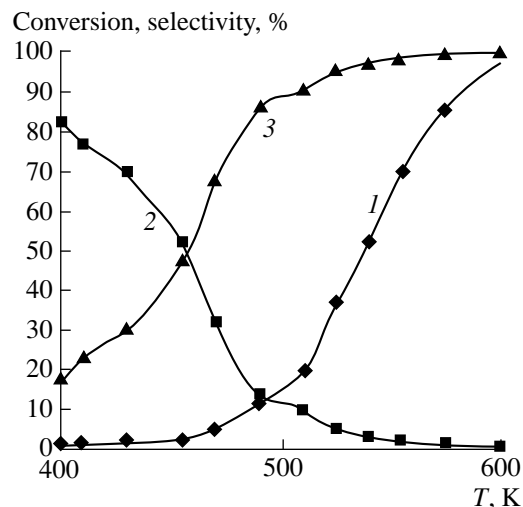
Presently, it seems to be settled that the adsorption of benzene occurs by a dissociative mechanism in many cases [22–25]. Thus, for example, deuterium exchange in a benzene molecule is represented as follows [26]:



Initially, the benzene molecule forms a  $\pi$ -complex with the active site (Z) of a catalyst; the aromatic ring in this  $\pi$ -complex is arranged parallel to the surface. In



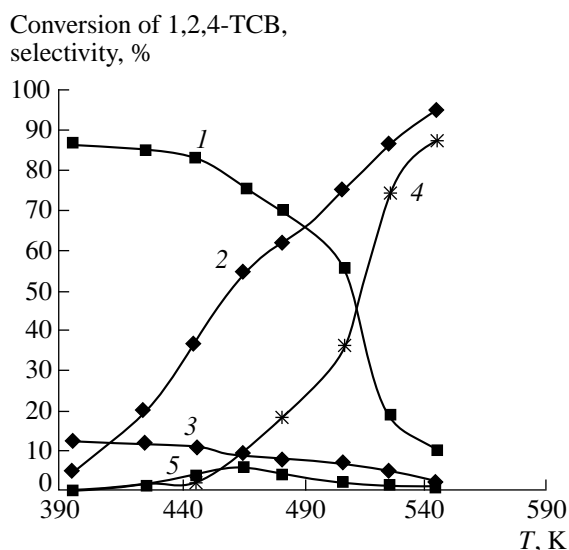
**Fig. 3.** Time dependence of the concentrations of 1,2,4,5-tetraCB hydrogenolysis products after the removal of hydrogen from the reaction mixture and the helium blowing of the catalyst: (1) 1,2,4-TCB, (2) benzene, (3) 1,2-DCB, and (4) 1,4-DCB.



**Fig. 4.** Temperature dependence of (1) 1,2-DCB conversion in the hydrogenolysis on a nickel–chromia catalyst and selectivity to (2) chlorobenzene or (3) benzene. The concentrations of hydrogen and 1,2-DCB in the starting reaction mixture were  $1.7 \times 10^{-3}$  and  $1.1 \times 10^{-3}$  mol/l, respectively; the space velocity was  $2400 \text{ h}^{-1}$ .

the course of the reaction, the molecule turned through  $90^\circ$  and the  $\pi$ -complex transformed into a  $\sigma$ -complex with the subsequent elimination of hydrogen or deuterium. The chemisorbed phenyl group reacts with the chemisorbed deuterium atom and reverts to a  $\pi$ -bonded state. These processes can be repeated several times until molecules desorb from the catalyst surface.

Dissociative adsorption was also supported by studies of halogen atom exchange in halobenzenes for a

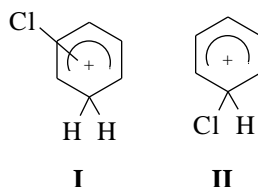


**Fig. 5.** Temperature dependence of (2) 1,2,4-TCB conversion in the hydrogenolysis on a nickel-chromia catalyst and selectivity to products: (1) 1,2-DCB, (3) 1,4-DCB, (4) benzene, and (5) chlorobenzene. The concentration of 1,2,4-TCB in hydrogen was  $9 \times 10^{-4}$  mol/l, and the space velocity was  $2400 \text{ h}^{-1}$ .

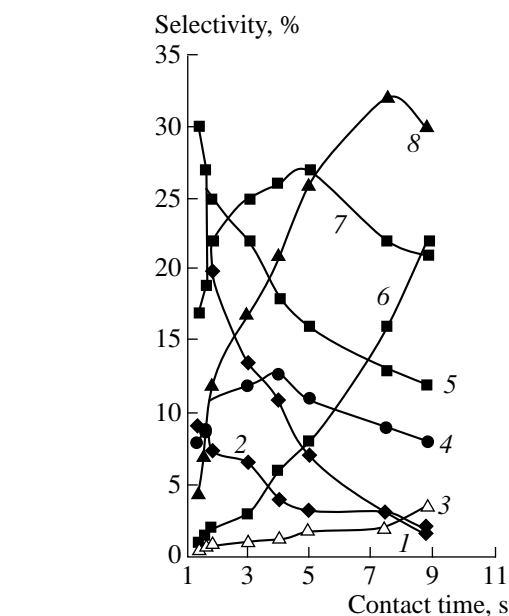
hydrogen atom from another molecule in the presence of a heterogeneous catalyst [9, 27].

Note that H/D isotope exchange in the deuterated benzene molecule  $\text{C}_6\text{H}_5\text{D} + \text{H}_2 = \text{C}_6\text{H}_6 + \text{HD}$  is analogous to the chlorobenzene hydrogenolysis  $\text{C}_6\text{H}_5\text{Cl} + \text{H}_2 = \text{C}_6\text{H}_6 + \text{HCl}$ .

In the presence of a chlorine atom at a benzene ring, several types of  $\sigma$ -complexes can be formed:



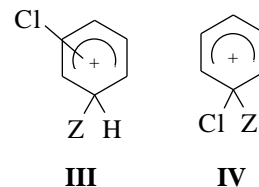
We performed quantum-chemical calculation of various  $\sigma$ -complexes by the SCF method in the MNDO semiempirical approximation [28] using the program described in [29]. We chose this calculation method because it is parameterized [28] for the correct reproduction of the corresponding characteristics of molecular structures. This calculation demonstrated that the C-Cl distance decreases in  $\sigma$ -complex **I** and increases



**Fig. 6.** Selectivities to products as functions of contact time in the hydrogenolysis of hexachlorobenzene on a nickel-chromia catalyst at 440 K: (1) PCB, (2) 1,2,4,5-tetraCB, (3) CB, (4) 1,2,4-TCB, (5) 1,2,3,4-tetraCB, (6) benzene, (7) 1,2,3-TCB, and (8) 1,2-DCB.

in  $\sigma$ -complex **II**, compared with the corresponding value in the chlorobenzene molecule (1.793 and 1.752 Å, respectively). This suggests that complex **II** exhibits a maximum probability of abstracting the chlorine atom. The results of calculation are consistent with data published by Manion and Louw [30]. They found that the addition of a deuterium atom to a chlorobenzene molecule at carbons bonded with hydrogen atoms is reversible, whereas the addition to a carbon atom bonded with chlorine is irreversible because it results in the elimination of chlorine and its replacement with deuterium.

It is reasonable to suggest the same tendency toward changing the C-Cl bond lengths in the  $\sigma$ -complexes



formed by chlorobenzene with the catalyst active site Z. The preferable formation of a  $\sigma$ -complex at the carbon

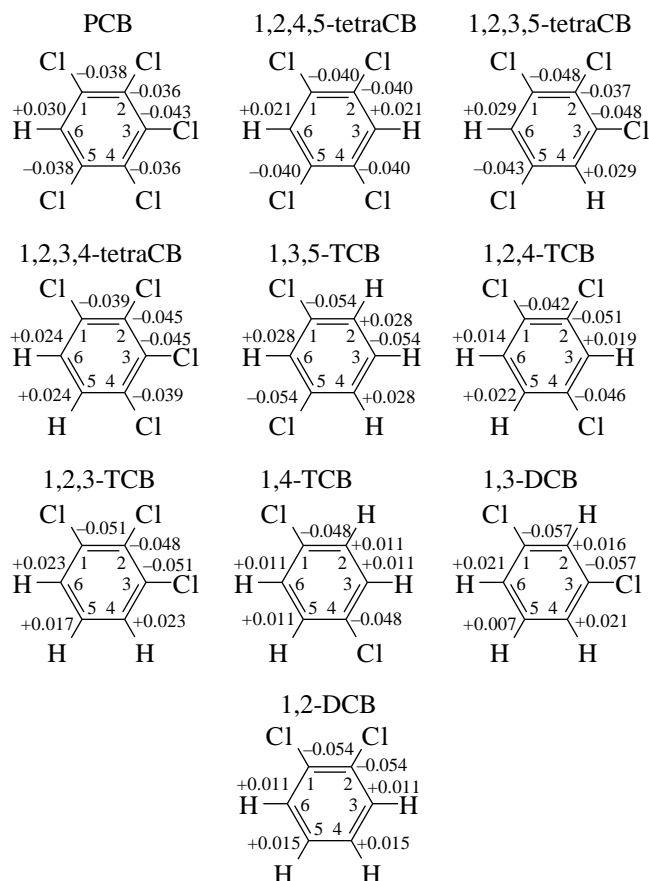
Orders of reaction with respect to substances and activation energies of chlorobenzene hydrogenolysis reactions

Reaction parameter	Substance				
	$\text{C}_6\text{H}_5\text{Cl}$	$1,2\text{-C}_6\text{H}_5\text{Cl}_2$	$1,2,4\text{-C}_6\text{H}_5\text{Cl}_3$	$1,2,4,5\text{-C}_6\text{H}_5\text{Cl}_4$	$\text{C}_6\text{Cl}_6$
Order with respect to initial substance	0.4	0.3	0.4	0.3	0.8
Order with respect to hydrogen	0.5	0.4	0.5	0.3	0.2
Activation energy, kJ/mol	$75 \pm 4$	$71 \pm 4$	$75 \pm 6$	$62 \pm 5$	$56 \pm 4$

atom with a maximum electron density in the aromatic ring is expectable. This problem was considered in a qualitative manner by Hagh and Allen [21] for homogeneous polychlorobenzene hydrogenolysis. They suggested that stable and unstable  $\sigma$ -complexes are formed in hydrogenolysis.

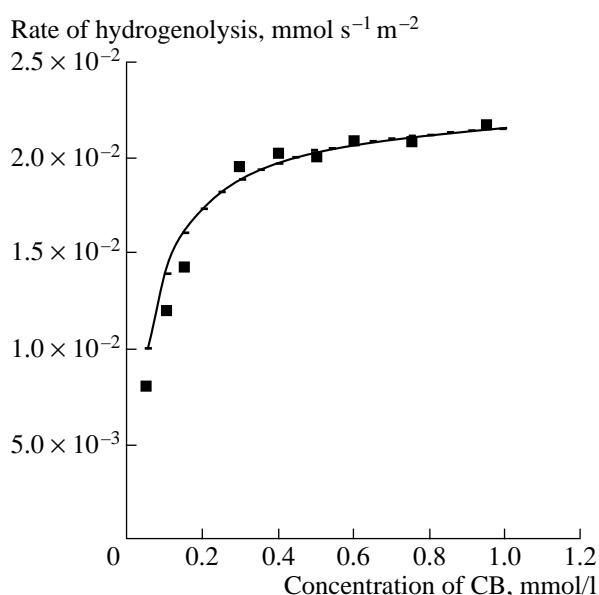
To test this hypothesis, we calculated electron densities at carbon atoms for various chlorobenzenes using the above method [28, 29].

*Electron Densities at Carbon Atoms  
in Chlorobenzenes*



We assume that the  $\sigma$ -complex of a catalyst and a chlorinated benzene molecule is primarily formed at an aromatic-ring carbon atom with the highest electron density. On this assumption, the calculation data suggest that, the hydrogenolysis of PCB, in which the carbon atom in the 3-position exhibits a maximum electron density, will result in the formation of 1,2,4,5-tetraCB in a greater amount. For the same reason, 1,3,5-TCB and 1,3-DCB will not be formed from the corresponding chlorobenzenes. The results of quantum-chemical calculations are consistent with assumptions made in [21] on the stability of  $\sigma$ -complexes.

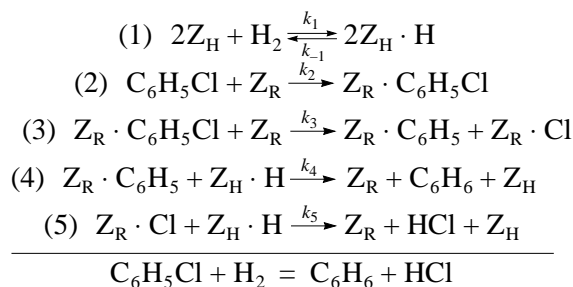
Indeed, in the products of hexachlorobenzene hydrogenolysis, 1,2,4,5-tetraCB predominates over other tetrachlorobenzenes, 1,2,4-TCB predominates over other trichlorobenzenes, and 1,2-DCB predominates over other dichlorobenzenes, whereas such chlo-



**Fig. 7.** Reaction rate of CB hydrogenolysis on a nickel-chromia catalyst at 400 K and a space velocity of 2400 h<sup>-1</sup> as a function of CB concentration in hydrogen.

robenzenes as 1,2,3,5-tetraCB, 1,3,5-TCB, and 1,3-DCB are not formed at all.

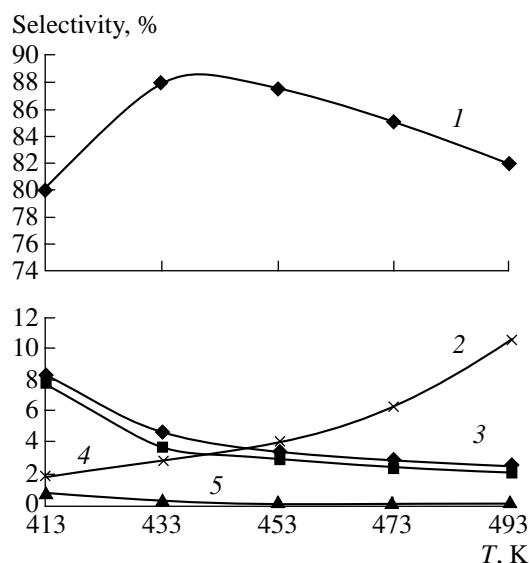
Taking into account the above facts and the results of kinetic studies on the hydrogenolysis reactions of chlorobenzenes, we suggest the following mechanistic scheme for chlorobenzene hydrogenolysis:



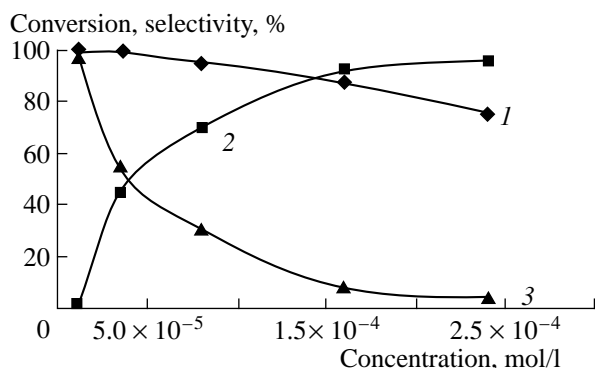
( $Z_R$  denotes the sites of chlorobenzene adsorption).

The above scheme of chlorobenzene hydrogenolysis is consistent with the Langmuir-Hinshelwood mechanism. It takes into account the experimental data that dissociated hydrogen is firmly bound to the surface in the presence of chemisorbed chlorine on the catalyst surface. The difference of the proposed scheme from known mechanisms [3] is that it considers active sites of two types on the catalyst surface; hydrogen is related to one of them ( $Z_H$ ), and chlorobenzene is related to the other ( $Z_R$ ).

Based on the mass action law and steady-state conditions, we found the following expression, which



**Fig. 8.** Temperature dependence of selectivities to products in the hydrogenolysis of hexachlorocyclohexanes (initial hexachlorocyclohexane concentration in hydrogen,  $1.6 \times 10^{-4}$  mol/l; space velocity,  $470 \text{ h}^{-1}$ ): (1) CB, (2) benzene, (3) 1,2-DCB, (4) 1,4-DCB, and (5) 1,2,4-TCB.



**Fig. 9.** Effect of the concentration of hexachlorocyclohexanes in hydrogen on (1) their conversion and selectivity to (2) chlorobenzene or (3) benzene at 413 K and a space velocity of  $750 \text{ h}^{-1}$ .

relates the rate of chlorobenzene hydrogenolysis ( $w_{\text{CB}}$ ) to the concentration of chlorobenzene in hydrogen:

$$w_{\text{CB}} = \frac{k_2 k_4 k_5 m (k_3 - k_2 C) C}{k_3 (k_4 k_5 m + k_2 C (k_4 + k_5))}, \quad (2)$$

where  $k_i$  are the rate constants of the corresponding steps,  $\text{l s}^{-1} \text{ mol}^{-2}$ ;  $C$  is the concentration of chlorobenzene,  $\text{mmol/l}$ ;  $m = (b C_{\text{H}})^{0.5} / (1 + (b C_{\text{H}})^{0.5})$ ,  $b = k_1 / k_{-1}$ ; and  $C_{\text{H}} = 44.68 \text{ mmol/l}$ .

The rate constants of reaction steps were optimized. For the hydrogenolysis of chlorobenzene at 400 K (Fig. 7), the following calculated values of constants gave the best fit to the experimental data:  $k_1 / k_{-1} = 0.054$ ,  $k_2 = 0.355$ ,

$k_3 = 3 \times 10^8$ ,  $k_4 = 3.65$ , and  $k_5 = 0.038$ . These results indicate that the interaction between the surface compounds  $Z_{\text{R}} \cdot \text{Cl}$  and  $Z_{\text{H}} \cdot \text{H}$  (step (II.5)) followed by the desorption of the resulting hydrogen chloride is the slowest step in the course of chlorobenzene hydrogenolysis.

The hydrogenolysis reaction of a mixture of hexachlorocyclohexane isomers was studied on the same nickel-chromia catalyst sample. The reaction was performed at 413–493 K. Note that the complete conversion of all starting isomers was attained at a total hexachlorocyclohexane concentration of  $1.6 \times 10^{-4} \text{ mol/l}$ , a space velocity of  $470 \text{ h}^{-1}$ , and a temperature of 413 K. Chlorobenzene was the main reaction product. Benzene, 1,2-DCB, 1,3-DCB, and 1,2,4-TCB were formed in considerably smaller amounts. It is interesting that in the absence of a catalyst, the conversion of hexachlorocyclohexanes, began only above 573 K, and 1,2,4-TCB was formed for the most part [31]. Figure 8 indicates that, as the temperature increased, the selectivities to dichlorobenzenes and 1,2,4-TCB decreased, whereas the selectivity to benzene increased, and the selectivity to chlorobenzene passed through a maximum. It is typical that the composition of reaction products depends on the concentration of hexachlorocyclohexanes: as the concentration in hydrogen was increased, the selectivity to chlorobenzene increased, whereas the selectivity to benzene decreased (Fig. 9).

Note that, upon the replacement of hydrogen with helium in the reaction mixture, the conversion of hexachlorocyclohexanes decreased; the selectivity to 1,2,4-TCB increased, and the selectivities to chlorobenzene and benzene dramatically decreased. The catalyst activity was completely restored on the subsequent replacement of helium by hydrogen. It is likely that the drop of the catalyst activity and changes in the selectivities to products are associated with an initial dehydrochlorination on the catalyst surface to form 1,2,4-TCB and hydrogen chloride, which is firmly bound to the surface. The presence of hydrogen in the reaction mixture not only facilitates the displacement of hydrogen chloride from the catalyst surface, but also is responsible for the hydrogenolysis of the resulting trichlorobenzene to less chlorinated benzenes. Tavoularis and Keane [32] observed such a phenomenon in their study of cyclohexyl chloride conversion on a  $\text{Ni/SiO}_2$  catalyst in the presence of hydrogen at 423–523 K. They found that cyclohexene was the main product (>97%), whereas only trace cyclohexane was detected. In the case of polychlorobenzene hydrogenolysis, the reaction occurs via the consecutive replacement of chlorine atoms by hydrogen in the molecule, whereas the reaction with hexachlorocyclohexanes occurs via the elimination of hydrogen chloride.

Thus, the results of this study suggest that different mechanisms are responsible for the removal of chlorine from the molecules of chlorine-containing benzenes and cyclohexanes.

## REFERENCES

1. Ovchinnikov, V.I., *Proizvodstvo kaprolaktama* (Caprolactam Manufacturing), Moscow: Khimiya, 1977.
2. Germain, J., *Catalytic Conversions of Hydrocarbons*, London: Academic, 1969.
3. Zhanaveskin, L.N., Aver'yanov, V.A., and Treger, Yu.A., *Usp. Khim.*, 1996, vol. 65, no. 7, p. 667.
4. Popov, S.A., Zhanaveskin, L.I., Ruban, S.G., et al., *IV Vsesoyuznaya nauchnaya konferentsiya "Sovremennoe sostoyanie i perspektivy razvitiya teoreticheskikh osnov proizvodstva khlororganicheskikh produktov"* (IV All-Union Scientific Conf. "Present State of the Art in Theoretical Foundations of Chlorinated Organic Product Synthesis), Baku, 1985, p. 179.
5. Moreau, C., Aubert, C., Durand, R., et al., *Catal. Today*, 1988, vol. 4, p. 117.
6. Moreau, C., Joffre, J., Saenz, C., et al., *J. Catal.*, 1990, vol. 122, no. 2, p. 448.
7. Vlasenko, V.M., *Kataliticheskaya ochistka gazov* (Catalytic Purification of Gases), Kiev: Tekhnika, 1973.
8. Lee, E.L., Sabatka, J.A., and Selwood, P.W., *J. Am. Chem. Soc.*, 1957, vol. 79, no. 20, p. 5391.
9. Eur. Patent 233035.
10. Korneichuk, G.P., Ostapyuk, V.A., and Boldyreva, N.A., *Kataliz i katalizatory* (Catalysis and Catalysts), 1984, no. 22, p. 77.
11. Estelle, J., Ruz, J., Cesteros, Y., et al., *J. Chem. Soc., Faraday Trans.*, 1996, vol. 92, no. 15, p. 2811.
12. Prati, L. and Rossi, M., *Appl. Catal., B*, 1999, vol. 23, no. 2, p. 135.
13. Srinivas, S.T., Lakshmi, L.J., Lingaiah, N., et al., *Appl. Catal., A*, 1996, vol. 135, no. 2, p. L201.
14. Creighton, E.J., Burgers, M.H.W., Jansen, J.C., et al., *Appl. Catal., A*, 1995, vol. 128, p. 275.
15. Snagovskii, Yu.S., Lyubarskii, G.D., and Ostrovskii, G.M., *Dokl. Akad. Nauk SSSR*, 1965, vol. 161, no. 1, p. 132.
16. Evzerikhin, U.I. and Lyubarskii, G.D., *Kinet. Katal.*, 1966, vol. 7, no. 6, p. 1085.
17. Pavlenko, N.V., Tripol'skii, A.I., and Golodets, G.I., *Kinet. Katal.*, 1989, vol. 30, no. 6, p. 1371.
18. Gaidai, N.A., Gudkov, B.S., Aliev, Kh.Kh., et al., *Kinet. Katal.*, 1992, vol. 33, no. 2, p. 457.
19. Janz, J., *J. Chem. Phys.*, 1954, vol. 22, no. 4, p. 751.
20. Kistiakowsky, G.B., Ruhoff, J.R., Smith, H.A., et al., *J. Am. Chem. Soc.*, 1936, vol. 58, p. 146.
21. Hagh, B.F. and Allen, D.T., *Chem. Eng. Sci.*, 1990, vol. 45, no. 8, p. 2701.
22. Fried, C.M., *Springer Scr. Surf. Sci.*, 1988, vol. 17, p. 67.
23. Graen, H.H., Neumann, M., Wambach, J., et al., *Chem. Phys. Lett.*, 1990, vol. 165, no. 2-3, p. 137.
24. Bhattacharya, A.K., *J. Chem. Soc., Faraday Trans. 1*, 1980, vol. 76, no. 1, p. 126.
25. Belokopytov, Yu.V., Grebennikov, Yu.N., and Korneichuk, G.P., *React. Kinet. Catal. Lett.*, 1981, vol. 16, no. 6, p. 409.
26. Garnett, J.L. and Sollich-Baumgartner, W.D., *Adv. Catal.*, 1966, vol. 16, p. 95.
27. Kiyonori, S. and Kensci, Y., *Nippon Kagaku Kaishi*, 1989, vol. 12, p. 1999.
28. Dewar, M.I.S. and Thiel, W., *J. Am. Chem. Soc.*, 1977, vol. 99, no. 15, p. 4899.
29. Pilipenko, A.T., Zaets, V.A., Khavryuchenko, V.D., et al., *Zh. Strukt. Khim.*, 1987, vol. 28, no. 5, p. 155.
30. Manion, J.A. and Louw, R., *J. Phys. Chem.*, 1990, vol. 94, p. 4127.
31. Bezobrazov, Yu.N. and Molchanov, A.V., *Geksakhloran* (Hexachloran), Moscow: Goskhimizdat, 1949, p. 144.
32. Tavoularis, G. and Keane, A.M., *Appl. Catal., A*, 1999, vol. 182, no. 2, p. 309.
33. Golodets, G.I., *Geterogenno-kataliticheskie reaktsii s uchastiem molekulyarnogo kisloroda* (Heterogeneous Catalytic Reactions with Molecular Oxygen), Kiev: Naukova Dumka, 1977.
34. Kiperman, S.L., *Vvedenie v kinetiku geterogennykh kataliticheskikh reaktsii* (Introduction to Kinetics of Heterogeneous Catalytic Reactions), Moscow: Nauka, 1964.