Reviews

Catalytic hydrodehalogenation of organic compounds

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Recent results on hydrodehalogenation (HDH) of alkyl halides, freons, aryl halides, polychlorinated derivatives of benzodioxines and biphenyls, and other compounds in the presence of heterogeneous and homogeneous catalysts are generalized. Effective and selective hydrodehalogenation proceeds *via* anion or radical anion intermediates. Special attention is given to the nature of the source of the hydrogen replacing the halogen.

Key words: catalytic hydrodehalogenation, organohaloderivatives, freons, polychlorinated dioxines and biphenyls.

Hydrodehalogenation (HDH) of organic compounds is a complex scientific problem combining fundamental and applied aspects. The practical aspects of HDH have recently become important, because the world community is anxious about the increasing contamination of the environment. Polychlorosubstituted organic compounds (dioxines, polychlorinated biphenyls, and others) are the most abundant and, at the same time, the most dangerous by-products of several large-scale industrial processes. Polyhaloalkanes (freons) are dangerous for the ozone layer of the Earth. It is not a coincidence that the predominant number of the recent works on this subject has been devoted to the dehalogenation and hydrogenolysis of just these compounds. Catalytic hydrodehalogenation makes it possible to decompose halogen-containing organic compounds and, in many cases, to obtain useful products. Progress in the study of catalytic hydrodehalogenation can be achieved when the possible reaction mechanisms are clear.

Analysis of recently published works shows that catalytic hydrodehalogenation is developing rapidly compared to other fields of chemistry. A detailed review[1] published in 1980 and devoted to hydrogenolysis of organic halides gives a good view of the state of the problem to that date. However, methodical approaches to this problem have changed considerably in recent years. For example, biodehalogenation is being rapidly developed, but it was not even mentioned in the review.[1] The considerable advances in biodehalogenation are associated with the elucidation of the chemical nature of the active factors of enzymes (dehalogenases) rather than of microorganisms, which makes it possible to model the action of enzymes by complex metal-containing catalysts. In the next century, the development of chemical industry will be probably based on the combination of chemical catalysis and biocatalysis in industrial fine organic synthesis and on the use of synthetic enzymes.[2] Photocatalysis has also intensely developed, and considerable success has been achieved in the use of photo- and electrochemical methods for hydrogenolysis of *C*-halogen bonds. Recently published patents are evidence that catalytic dehalogenation is performed on both laboratory and industrial scales.

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Despite the progress achieved, many aspects of the mechanisms of catalytic hydrodehalogenation are not yet clear. Anion, radical, and radical anion mechanisms of hydrodehalogenation have been suggested depending on various conditions and catalysts. Taking into account basic differences in reaction conditions (for example, both gaseous hydrogen and organic hydrogen-containing donor molecules can serve as a hydrogen source; the presence or absence of electron transferring agents, counterions in the case of complex catalysis, *etc.*, in the reaction system), mechanisms can also be different in each particular case.

In this review, we have attempted to generalize the results of the last decade of study of the conditions and mechanisms of catalytic HDH of organic substances.

1. Hydrodehalogenation of aliphatic halides

Predominantly metal-containing, less frequently, nonmetallic catalysts as well as homogeneous and heterogenized metal complexes modeling enzyme action are used for HDH of aliphatic halides.

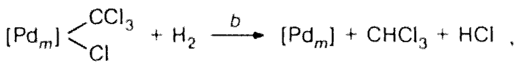
1.1. Hydrodehalogenation in the presence of heterogeneous catalysts based on group VIII metals

Group VIII metals are widely used for hydrodechlorination (HDC) of alkyl halides. The methods of reductive HDC of organic halides in the presence of catalysts of heterogeneous hydrogen transfer are patented. Polychloromethanes dechlorinate in the presence of a group VIII or group IB metal supported by aluminum oxide. The selectivity of the reaction can depend on the dispersity of the support and the content of the active component. For example, in the presence of the catalyst 0.5 % Pt/Al_2O_3 on a support with a developed surface (θ-Al_2O_3, specific surface 133 $m^2\ g^{-1}$), the selectivity is 71 % with respect to $CHCl_3$ [3] (θ-Al_2O_3 is formed in the calcination of α-Al_2O_3 at 800 to 900 °C from γ- or η-Al_2O_3 and possesses a lower Lewis acidity). At the same time, for a similar catalyst on a support with a less developed surface (the surface of the α-Al_2O_3 support is 80 $m^2\ g^{-1}$), the conversion of CCl_4 is high and stable: 92.7 % after 118 h at a selectivity of 83 % with respect to $CHCl_3$. A higher selectivity with respect to chloroform is achieved for the modification of this catalyst with a lanthanide group metal oxide. For example, in the presence of Pt(0.25 %)LaO(5 %)/Al_2O_3 at a molar ratio $CCl_4 : H_2 = 0.1$ and at a low temperature (120 °C), and a high volume rate (3000 h^{-1}), 88 % $CHCl_3$ is formed for a selectivity of 92 %.[4] When the content of Pt in Pt/Al_2O_3 catalysts increases from 0.4 to 3 wt. %, the selectivity with respect to chloroform increases from 40 to 85 % at a constant rate calculated per Pt atom.[5]

The reduction of CCl_4 is possible even in a mixture with CO_2. For example, at 160 °C a $H_2 : CO_2 : CCl_4 = 2 : 1 : 1$ mixture was passed over the Pd/C catalyst. When the contact time was 20 s, a mixture of products of complete and partial dechlorination was formed: 62 % CH_3Cl, 29 % CH_2Cl_2, and 9 % CH_4.[6]

Hydrodechlorination of CCl_4 under the action of hydrogen in the presence of $Pd(OAc)_2$ in the liquid phase (solutions in acetic acid) at 20 to 80 °C results in the formation of methane.[7] In this case, the catalyst is palladium black formed in the reduction of $Pd(OAc)_2$ with hydrogen under the reaction conditions. The authors mention that the introduction of polar solvents into the reaction medium results in an increase in the HDC rate and a decrease in conversion. For example, methane was the main product in the presence of DMFA, dioxane, and benzyl alcohol; a mixture of chloroform and chloromethane was the main product in the presence of isopropanol; while a mixture of chloroform, chloromethane, and methane was formed in the presence of *tert*-butanol. In the latter case, an unusual order of the change in the selectivity of the reaction over time is observed. The yield of CH_4 passes through a maximum (40 %, 60 min) and then decreases almost to zero (3 to 4 h), and the yield of chloroform increases monotonically to 75 % (4 h). A yield of chloromethane rapidly increases (to 25 %) for 1 h and then is stabilized. The authors[7] believe that this is related to the existence of an initial period of formation of the catalytically active complex. We believe than one should speak more exactly about a change in the nature of the catalytic system rather than about its formation in the initial period of the reaction. The mechanism suggested by the authors includes a fast reversible reaction of the catalytic active centers with CCl_4 followed by the slow hydrogenolysis of the complex formed:

$$[Pd_m] + CCl_4 \overset{a}{\rightleftharpoons} [Pd_m]\genfrac{}{}{0pt}{}{\diagup CCl_3}{\diagdown Cl}\ , \qquad (1)$$



$$[Pd_m]\genfrac{}{}{0pt}{}{\diagup CCl_3}{\diagdown Cl} + H_2 \xrightarrow{b} [Pd_m] + CHCl_3 + HCl\ , \qquad (2)$$

a, rapidly; *b*, slowly.

Other transformations leaving the chloromethyl group bound to the catalyst can occur in parallel with hydrogenolysis (2), and result in an increase in the depth of HDC. However, the presence of the solvent is not taken into account in this scheme, and alcohols, as will be shown below, can participate directly in HDC, being donors of hydrogen as well.

The relatively fast reductive dechlorination of CCl_4 and $CHCl_3$ in aqueous solutions occurs in the presence of finely dispersed metallic iron under anaerobic conditions at room temperature.[8] The reaction occurs sequentially, and the rate of HDC sharply decreases for each succeeding stage. For example, CCl_4 is transformed into $CHCl_3$ after 2 to 2.5 h, while the half-transformation of $CHCl_3$ to CH_2Cl_2 occurs only after 100 h. Studying the kinetic regularities of this reaction, the authors have shown that of three possible mechanisms of HDC (direct transfer of an electron from Fe^0 to the absorbed substrate, reduction by dissolved Fe^{2+}, and reduction by hydrogen formed due to the corrosion of iron in the presence of iron as a catalyst), the first mechanism is the one that occurs:

$$Fe^0 + RX + H^+ \longrightarrow Fe^{2+} + RH + X^-.$$

The reaction rate is limited by the diffusion of the substrate to the iron surface. However, under anaerobic conditions, these regularities can be distorted, and the distortions can be very substantial in the purification of sewage.

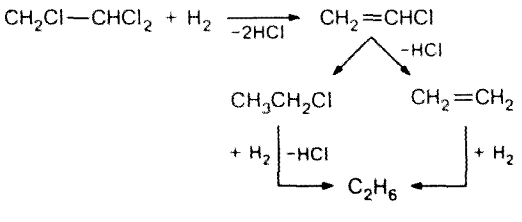
Possible mechanisms of the reductive catalytic dechlorination of polychlorinated ethanes (1,2-dichloroethane, 1,1,2-tetrachloroethane, and 1,1,1-trichloroethane) in the presence of palladium-supported catalysts (mainly, industrial 0.5 % $Pd/\gamma\text{-}Al_2O_3$) at 200 to 350 °C in a hydrogen atmosphere have been discussed.[9] Ethane and ethylene were the main products in almost the whole temperature range, and the content of partially dechlorinated products (both saturated and unsaturated) turned out to be anomalously low. The authors believe that this composition of products can be explained within the framework of the suggested mechanism of HDC of vicinal di- and polychloroalkanes, according to which the reaction begins with dechlorination to form an unsaturated compound, which then can be rapidly hydrogenated under the reaction conditions, for example, for 1,1-dichloroethane, according to the scheme:

$$CH_2Cl-CH_2Cl + H_2 \xrightarrow{i} CH_2=CH_2 + 2HCl,$$

$$CH_2=CH_2 + H_2 \xrightarrow{i} C_2H_6$$

i. Catalyst.

In fact, when the reaction temperature increases from 250 to 300—350 °C, the yield of ethane decreases from 90—100 to 75 %, and the yield of ethylene increases due to a decrease in the rate of its hydrogenation. In the transformation of 1,1,2-trichloroethylene *via* this mechanism, vinyl chloride should be the first product, however, its yield is insignificant (1—2 %) and does not increase as the reaction temperature increases, which is associated by the authors with fast hydrogenation and HDC to ethyl chloride and ethylene, respectively:



It is clear that HDC of geminal halogen-substituted compounds, for example, 1,1,1-trichloroethane, should occur *via* a different mechanism, probably with subsequent replacement of chlorine with hydrogen. In fact, the composition of the products is different in this case (mainly, ethane and 1,1-dichloroethane), and when the reaction temperature increases from 200 to 350 °C the yield of ethane decreases from 94 to 51 %, and the yield of 1,1-dichloroethane increases from 4 to 26 %.

It has been established[10] in a study of HDC of five chlorinated ethylenes, including tetrachloroethylene and vinyl chloride, in the presence of 0.5 % Pd supported by C or Al_2O_3 in an H_2 atmosphere (0.1 atm) at ~20 °C, that ethane is the main product (the other products were not identified). The yield of ethane with the use of Pd/Al_2O_3 (85 %) is higher than that in the presence of Pd/C (55 %). The reaction is first-order with respect to both the substrate and the metal. The presence of oxygen sharply decreases the efficiency of HDC; however, the nature of this phenomenon was not studied in Ref. 10.

The Pd/C catalyst has been used for dechlorination of freon 114a (1,2,2,2-tetrafluoro-1,1-dichloroethane) to freon 134a (1,2,2,2-tetrafluoroethane)[11] and for dehalogenation of other organic halides at 50 to 150 °C and $p_{H2} < 4$ atm in the presence of alkali in an alcohol solution.[12] The palladium catalyst was also used for selective removal of chlorine in the CF_3CClF_2 molecule in the presence of other halohydrocarbons. For example, in a mixture with a molar ratio $H_2 : CF_3CClF_2 : CH_3CClF_2 = 2 : 1 : 0.3$ at 250 °C, CF_3CClF_2 transforms to CF_3CHF_2 with a selectivity of 99.8 % at a conversion of 65 %.[13]

To change the activity and especially the selectivity of palladium catalysts (whose selectivity is comparatively low), modifications with other metals are widely used in HDC of freons. Modifying the palladium catalyst with silver, as should be expected, decreases the depth of dechlorination of CCl_2FCClF_2 (R-113). At 275 °C in the presence of reduced Pd—Ag/C in a hydrogen atmosphere, R-113 transforms in 30 min to chlorotrifluoroethylene with a selectivity of 56 % at a conversion of 49.5 %.[14]

Modifying a palladium or rhodium catalyst with copper[15] makes it possible to achieve high values of selectivity of hydrodehalogenation. For example, chloroform is formed from CCl_4 in a yield of 52.8 % at 100 % conversion in the presence of a carbon-supported catalyst containing 10 % copper, 0.044 % rhodium, and 6.5 % methyltriphenylphosphonium chloride.

Palladium catalysts supported by aluminum oxide (5 % Pd/Al_2O_3 and 0.5 % Pd/Al_2O_3) were modified with 26 metals with the purpose of enhancing their selectivity.[16] In choosing a modifying agent, the authors of this work tried to suppress the further reduction of double bonds and to obtain unsaturated compounds (chlorotrifluoro- and trifluoroethylene) that can serve as monomers in the production of Teflons. Trifluoroethylene

Table 1. Effect of modification on the activity and selectivity of 5 % Pd/Al_2O_3 system in the hydrodechlorination of freon R-113 by hydrogen[16]

Modifying agent	M/Pd (at.)	T/K	Conversion (%)	Selectivity (%)	
				3FCl	3FH
—	0	423	20	0	10
$TlNO_3$	2	473	13	100	0
	1	473	34	98	2
	0.5	473	60	1	72
$SnCl_2$	1	503	12	78	17
		523	21	70	24
$Cu(NO_3)_2$	2	473	45	37	43
$InCl_3$	1	503	15	90	0
$CdCl_2$	4*	473	8	64	10
		523	21	54	27
$AgNO_3$	1	473	44	59	33
	4*	473	12	70	28
$Pb(NO_3)_2$	1	473	24	51	43
$HgCl_2$	2	473	31	17	80
$BiCl_3$	2*	473	2	—	—
	0.4	473	46	12	86

* 0.5 % Pd/Al_2O_3.

is also an intermediate product in the synthesis of ozone-safe freon R-134a, which is used as a cooling agent. Metals of groups IB—IIIB (Ag, Bi, Cd, Cu, Hg, In, Pb, Sn, and Tl) exerted a positive effect on the selectivity with respect to trifluorochloro- and trifluoroethylene. The subsequent dechlorination of 1,1,2-trichlorotrifluoroethane to trifluorochloro- and then trifluoroethylene occurred on the obtained catalysts. As can be seen from Table 1, the maximum selectivity according to the amount of desirable products is achieved in the presence of $Bi-Pd/SiO_2$ and Tl—Pd/C, and changing the content of thallium in the catalyst results in a sharp predomination of one of the products (from 100 % chlorotrifluoroethylene to 72 % trifluoriethylene). High selectivity (about 80 %) is retained when the reaction temperature and degree of conversion change.

To elucidate the nature of the modifying action, the authors performed a thermodynamic analysis of the catalytic cycle. All efficient promoters fall in the same region in the plot of the dependence of the logarithm of the equilibrium constant for the transformation of HCl (3) on the logarithm of the equilibrium constant for the decomposition of the corresponding metal chloride (4).

$$MF_n + nHCl = MCl_n + nHF, \tag{3}$$

$$MCl_n + n/2\ H_2 = M + nHCl. \tag{4}$$

The data presented are evidence that the modifying agents act to suppress the hydrogenating activity of the platinum group metal and its activity in hydrodefluorination. It is shown using several physicochemical methods for studying catalysts that the activating action of a metal-modifying agent is achieved by decomposition of ensembles of palladium atoms. For example, in the modification with thallium, the broad peak of palladium in the X-ray photoelectron adsorption spectra of Tl—Pd/C shifts to lower 2θ angles, which attests to the formation of a thallium—palladium alloy or intermetallide.

Removal of iodine, bromine, and chlorine is possible on a rhodium catalyst in a hydrogen atmosphere, and only fluorine cannot be removed. When compounds of general formula $RCH_nCl_cBr_dI_e$ (where $R = C_aF_{(2a-b)}H_b$, $a = 1-4$, $b = 0-4$, $c, d, e = 0-3$, $n = 0-2$, $c + d + e = 3 - n$) are hydrogenated at a molar ratio hydrogen : substrate = 6 : 1 over Rh/SiO_2 and at temperatures of 450 °C in the first reaction zone and 220 °C in the second reaction zone, 97.3 % $(CF_3CH_2)_2$ is formed.[17]

In the presence of Pd/C and hydrogen at 350—600 °C, fluorine as well as chlorine is replaced by hydrogen: chloropentafluoroethane and 1,1,1,2-tetrafluoroethane (both individual and in a mixture) can be reduced to the corresponding fluoroalkanes and (or) hydrocarbons.[18] Hydrogenation of decafluoro-2-pentene with gaseous hydrogen in the presence of a platinum catalyst at 300 °C gives octafluoropentane with a selectivity of 90 %.[19] Catalytic hydrogenation of chlorofluorocarbons at high pressure in the liquid phase also gives good results. For example, in the presence of ethanol, Pd/C, and hydrogen (10 kg cm^{-2}) in an autoclave at 200 °C, 1,1,2-trichloro-1,2,2-trifluoroethane dechlorinates to 1,2-dichloro-1,2,2-trifluoroethane. The degree of conversion is 50—51 %, and remains almost unchanged when the duration of the experiment increases from 2 to 1000 h. At the same time, under similar conditions in the gaseous phase, the degree of conversion decreases from 70 to 30 % as the reaction time increases from 2 to 20 h.[20]

Interesting results were obtained in a study of the effects of 11 additives to the catalysts (0.5 and 5 % Pd/Al_2O_3) on HDC of 1,1,2-trifluoro-1,2,2-trichloroethane (freon R-113) to trifluoroethylene.[21] The maximum selectivity is observed in the presence of catalysts modified by Bi and Tl (78 and 70 % at 200—250 °C and yields of products of 44 and 39 %). The catalysts obtained by deposition of Pd—Bi on SiO_2 are more active in HDC: when the content of Pd is 2 % and the ratio Bi : Pd = 1 : 2, the selectivity is 90 % and the yield of trifluorochloroethylene is 99 %.

HDC of R-113 over Ni/TiO_2, $MnTiO_3$, and Ni and Co powders at 300 °C also results in the formation of trifluorotrichloroethylene, while in the presence of Pd/TiO_2 the main products are difluoroethylene and trifluoroethane.[22]

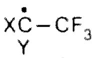
At temperatures higher than 150 °C, the main product of the transformation of R-113 in the presence of Pd/TiO_2 is difluoroethylene, while in the presence of Pd/C it is trifluoroethane (selectivity 85 %).[23] The activity of rhodium and platinum catalysts is lower than that of Pd/C. The authors of Ref. 23 found that the addition

Table 2. Activities of silica gel-supported metals reduced at 450 °C in HDC of R-113 in a flow-type system at the ratio Ar : H_2 : R-113 = 6 : 6 : 1, 1 g of catalyst, flow rate 65 cm^3 min^{-1} [24]

Composition (%)	$T_{50}{}^{a}$/°C	Selectivity (%)			
		316[b]	1316[c]	123[d]	143[e]
Pd (0.5)	317	0	0	17	80
Pt (5)	384	0	0	74	26
Ru (5)	408	7	80	3	3
Ni (10)	523	17	42	1	13

[a] Temperature corresponding to 50 % conversion. [b] $CF_3CCl_2CCl_2CF_3$. [c] *cis*- and *trans*-$CF_3CCl{=}CClCF_3$. [d] CCl_2H-CF_3. [e] CFH_2-CF_2H.

of up to 2 % water vapor to the reaction mixture suppresses the hydrogenolysis to methane.

In several works, transformations of freon R-113 on metal oxides and supported metallic catalysts were studied.[24] It was found that three chlorine atoms are successively replaced by hydrogen in the presence of catalysts based on Pd, Pt, Rh, and Ni. Dimerization of the partially dechlorinated molecules is possible along with HDC on nickel and ruthenium catalysts. As can be seen from Table 2, the maximum depth of dechlorination, as in Ref. 23, is achieved in the presence of a low-percentage palladium catalyst (up to 80 % of the completely dechlorinated product). In the presence of 5 % Pt/SiO_2, the depth of dechlorination is lower: 74 and 26 % of dichlorotrifluoroethane and trifluoroethane, respectively, are formed in a flow-type system. Nickel and rhodium catalysts give substantial amounts of dimerization products and chlorotrifluoroethane. According to the authors' opinion, the key step in the hydrodechlorination of both chlorofluorohydrocarbons and chlorofluorocarbons not containing hydrogen is dissociative adsorption followed by the formation of the radical  $\mathrm{X}\underset{\mathrm{Y}}{\dot{\mathrm{C}}}-\mathrm{CF_3}$ (X, Y = H, Cl, or F); however, no proofs of this mechanism are presented in the work.

In the presence of Ni/TiO_2 prepared by decomposition of Ti—Ni—H hydride systems with mineral acids, the main product of DHC of R-113 at 200—400 °C was chlorotrifluoroethylene, and the activity and selectivity of the catalysts strongly depended on the composition of the initial hydride.[25] The catalysts containing 8.3 % Ni prepared from hydride $TiNiH_{0.6}$ possess the maximum activity: at 300—350 °C the degree of conversion was 98 % at a selectivity of 95 %. The substantial differences in the activity of the catalysts prepared from intermetallide hydrides with different Ti : Ni ratios are explained by the authors by the existence of strong metal—support interaction in the system, and this approach seems promising for explanaining the strong effect of metal-modifying agents on the selectivity of HDC in the presence of supported metal-containing catalysts.

Catalysts prepared by impregnation and containing 5 % Pd on aluminum oxide, fluorinated aluminum oxide, or AlF_3, lead to hydrodechlorination of C_2F_5Cl to C_2F_5H in a hydrogen atmosphere with high conversion (100 %) and selectivity (97 %).[26]

Dehalogenation and even decomposition of halohydrocarbons occur on complex catalysts made up of a stable (toward the action of hydrogen halides) support of iron and (or) nickel alloys containing more than 15 % chromium covered with a titanium dioxide layer and impregnated with one or more of the following metals: Pd, Pt, Ru and Os, Re, and Ir.[27]

A study of the adsorption and decomposition of alkyl iodides on the Ni(100) surface at temperatures below 150 K showed that free alkyl radicals form on the surface, which then can desorb after destruction (at low degrees of coverage),[28] reduction, or by hydride displacement (at high degrees of coverage). The final product of this low-temperature reaction is a mixture of the corresponding alkane and alkene. Probably a radical mechanism is possible in this case due to the low energy of the C—I bond.

In the presence of Devard alloy in an aqueous-alcohol alkali, chloroform is hydrodechlorinated to methane with a low conversion rate (8.1 %), but a high selectivity (80 % with respect of methane).[29]

1.2. Hydrodehalogenation in the presence of bimetallic and nonmetallic catalysts

Nickel-chromium catalysts, including those on oxide supports, are used in oxidative dechlorination to form less halogenated olefins from the corresponding halo-substituted alkanes.[11,30,31] However, in some cases, reduced catalysts can lead to reductive dechlorination. For example, silica gel-supported iron, cobalt, nickel, and chromium have been used[31,32] as selective but low-active catalysts to remove one chlorine atom from 1,1,1-trifluoro-2,2,2-trichloroethane. Only 3.5 % 1,1,1-trifluoro-2,2-dichloroethane was obtained after 6 h at 450 °C.

A convincing argument in favor of the acid-base mechanism is the fact that reductive dehalogenation of organic compounds can occur on nonmetallic catalysts. For example, in the presence of active carbon in a hydrogen atmosphere at 200—700 °C and 0.5—10 bar, one or more chlorine or bromine atoms are removed from various organic compounds, including alkanes, cycloalkanes, alkenes, aromatic hydrocarbons, and ethers.[33]

HDC occurs better in the presence of carbon fiber activated by hydrogen at high temperatures (450 °C); such catalysts do not loose their activity and selectivity for several hours.[34] For example, at 350 °C in the presence of the catalyst FE—300 (carbon fiber based on polyacrylonitrile) pre-treated with hydrogen at 450 °C to remove contaminants, and at a convey or rate of 0.21 g min^{-1}, 1,2-dichloroethane is transformed into chloroethylene. After 6 h the conversion is 69.5 % at a selectivity of 98.9 %, and after 23.5 h it is 70.1 at a selectivity of 99.2 %.

Dechlorination of R-113 is observed in the presence of hydrogen at a molar ratio hydrogen : substrate = 3 and temperature 500 °C on spherical silica gel with a high specific surface (106 $m^2\ g^{-1}$) with considerable conversion and high selectivity (65 and 94 %, respectively).[35]

In the presence of zeolite catalysts, dechlorination of alkyl chlorides usually occurs along with dehydrogenation to form olefins or less chlorinated olefins. However, modifying zeolite with a metal catalyst of hydrogenation (for example, nickel), makes it possible to obtain hydrogen-saturated products as well. For example, Ref. 36 describes the complete HDC of haloderivatives of aliphatic hydrocarbons in a flow-type system in the presence of hydrogen and nickel-modified specifically selective zeolite (for example, Ni—ZSM5). This bifunctional catalyst combines the ability of nickel to catalyze hydrogenolysis of the C—Hal bond with the acidic and specifically selective properties of zeolite. The products contain only hydrogen halide and hydrocarbons, and the relative amounts of the obtained hydrocarbons of different classes (paraffins, olefins, aromatics) strongly depends on the gas : reactant ratio, volume rate, and temperature.

1.3. Hydrodehalogenation in the presence of complex catalysts. Modeling enzymatic dehalogenation

Triphenylphosphine and carboran rhodium complexes, both homogeneous and heterogenized on polymer supports, exhibit noticeable activity in HDC of chlorocyclopropane derivatives.[37] For example, in the presence of $RhCl(PPh_3)_3$, ethanol, and KOH, the initial rate of HDC of 3,3,7,7-tetrachlorotricyclo[4.1.0.$0^{2,4}$]heptane to 3-chlorotricyclo[4.1.0.$0^{2,4}$]heptane was 98 mol $(L\ min\ g\ Rh)^{-1}$. However, the complex rapidly decomposes and loses its activity. The complex heterogenized on a polymer support is less active (the initial rate of HDC is up to 24 mol $(L\ min\ g\ Rh)^{-1}$), but its action is stable.

Since the problem of the biological decomposition of haloorganic compounds is especially important, much attention has recently been given to modeling the action of the dehalogenase enzymes responsible for biodehalogenation by microorganisms.[38,39] Polychlorinated ethylenes (as well as aromatic compounds such as benzenes) undergo reductive dechlorination in the presence of vitamin B_{12}, coenzyme F_{430}, or hematin catalysts and a strong reducing agent, for example, Ti^{III} citrate or dithiothreitol.[40]

In Ref. 40, the complex Ni(tmtaa) (tmtaa is the 6,8,15,17-tetramethyl-5,14-dihydrodibenzo-[*b,i*](1,4,8,11)-tetraazacyclotetradecine dianion) is used as a model of the active center of the Me-coenzyme of M-reductase, factor F-430 (nickel complex of hydrogenated porphyrin). This complex is similar to metalloporphyrins, but the metal can easily change its degree of oxidation due to low conjugation. The authors consider the key stage to be the $Ni^{II} \to Ni^{I}$ reduction, and sodium borohydride is the reducing agent in this case. By means of this reductive system, iodine can be easily removed. Removal of bromine is more difficult, and chlorine almost cannot be removed in the corresponding halocyclohexanes. For example, in a diglyme—ethanol mixture at 30 °C at the ratio of Ni(tmtaa) : halocyclohexane : $NaBH_4$ = 1 : 50 : 100, the number of reaction cycles (the alkane : catalyst ratio) after 3 and 6 h was 0 and 0.01 for chlorocyclohexane, 11.3 and 17.9 for bromocyclohexane, 22.0 and 30.9 for iodocyclohexane, and 0.9 and 1.7 for 1-bromoadamantane. The reaction does not occur under the same conditions in the absence of the complex. The potentials of the reduction half-waves of 1-bromoadamantane and bromocyclohexane (−2.38 and −2.29) do not substantially differ; however, the activity of bromoadamantane in dechlorination is lower by one order of magnitude. In the authors' opinion, this testifies that the reaction mechanism is substantially more complicated than a simple electron transfer. It is likely that the elementary stage includes the nucleophilic replacement of halogen by a hydride ion similar to that in the noncatalytic reduction of alkyl halides by sodium borohydride. We drew similar conclusions in the study of the reduction of *gem*-dihalocyclopropanes by supported and complex rhodium catalysts.[41] For example, it was shown by the use of deuterosubstituted reagents that in the presence of rhodium triphenylphosphine complexes (homogeneous and heterogenized on silica gel modified by γ-aminopropyl groups) the replacement of halogen by a hydrogen atom of the solvent, most probably, the hydrogen atom at the α-position of the isopropanol molecule, is possible in *gem*-dichlorosubstituted derivatives of cyclopropanes.

The nucleophilic substitution mechanism was experimentally confirmed by deuterium-hydrogen exchange.[39] When the reaction was performed with bromocyclohexane in the presence of $NaBH_4$ and C_2D_5OD, a mixture of C_6H_{12} and C_6DH_{11} of composition 84 : 16 was formed; when C_2H_5OH and $NaBD_4$ were used, the composition of the mixture was the same at a molar ratio of 63 : 38. The following scheme was suggested on the basis of these data:

$$R{-}Br \xrightarrow[-Ni^{II}(tmtaa)]{[Ni^{I}(tmtaa)]^{-}} [R{-}Br]^{\overset{\cdot}{-}} \xrightarrow[-Br^{-}]{} R^{\cdot} \xrightarrow{H^{\cdot}\ (from\ solvent)} RH\ , \qquad (5)$$

$$R{-}Br \xrightarrow{D^{-}} RD + Br^{-}. \qquad (6)$$

According to this scheme, it is best to use a solvent that facilitates the elimination of Br^{-}, easily dissolves sodium borohydride, is not coordinated by nickel, and exhibits weak proton-donating properties, because the reduction of a proton to hydrogen is catalyzed by nickel complexes. The best solvent is diglyme—5 % ethanol.

The redox processes in the system are clearly illustrated by ESR. In the presence of sodium borohydride, the spectrum of Ni(tmtaa) contains a singlet signal characteristic of the Ni^I species ($g_\parallel = 2.26$, $g_\perp = 2.13$), which rapidly disappears due to the oxidation of the nickel species when bromocyclohexane is added to the system.

The reduction of Ni(tmtaa) by 2 % sodium amalgam gives the complex $Na^+[Ni^I(tmtaa)]^-$, whose ESR spectrum contains a strong signal ($g_\parallel = 2.10$, $g_\perp = 2.01$) substantially different from the signal of $Ni(tmtaa)/NaBH_4$. Therefore, an additional ligand is coordinated with nickel in the latter complex, and it is not BH_3, because although the addition of BH_3 in tetrahydrofuran changes the spectrum of $Na^+[Ni^I(tmtaa)]^-$, this new spectrum also differs from that of $Ni(tmtaa)/NaBH_4$. Therefore, it can be suggested that the additional ligand can be either H^- or BH_4^-. These data confirm the suggested[41] mechanism involving a hydride ion.

The authors of a recently published work[42] report for the first time on the homogeneous reaction of organometallic compounds of transition metals with substituted fluorocarbons. The organometallic anion $[C_pFe(CO)_2]^-$ leads the defluorination of perfluoromethylcyclohexane and perfluorodecalin at room or at lower temperatures in tetrahydrofuran. In the absence of hydrogen in the gas phase, $C_{10}F_{18}$ is formed, and at the addition of 6 eq. $C_pFe(CO)_2R$ the degree of conversion is 90 % with respect to the substrate (R is the perfluorodecalin fragment).

Cytochrome P450cam, whose crystal structure and oxidation cycle have been well studied,[43] was used as a catalyst for modeling processes occurring during the biological reductive dehalogenation of organic halides. Halosubstituted methanes or ethanes were used as substrates. To reduce cytochrome, a system must certainly contain electron donors, which can be organic or biological electron donors, for example, proteins or NADH. The products can be alkanes, alkenes, or carbenes, depending on the type of mechanism that occurs in the system: two-electron transfer followed by protonation, β-elimination, or α-elimination.

Vitamin B_{12} and other corrinoids catalyze the anaerobic reductive dehalogenation of CCl_4 and its lower homologs by Ti^{III} citrate to form methane.[44] The authors suggest that the reduction of $Co^{III}B_{12}{-}R$ results in the formation of an unstable radical anion intermediate $Co^{III}B_{12}{-}R^-$, and the C—Co bond breaks to form a molecule of the dehalogenation product. It is noteworthy, however, that the potential of the one-electron reduction of $Co^{III}B_{12}{-}CH_3$ is very negative (approximately −1.3 V in a dimethylformamide—propanol-1 mixture).

By analogy, fermentative anaerobic HDH was performed[45] using the catalytic TiO_2—CoTSP system (TSP is tetrasulfophthalocyanine), a hybrid catalyst combining a semiconductor and a macrocycle. Cobalt 4,4′,4″,4‴-tetrasulfophthalocyanine, which is structurally similar to cyancobalamine (vitamin B_{12}), has been studied considerably less.

Under homogeneous conditions, the reactions of Co^ITSP with CCl_4, $CHBr_3$, $CHClBr_2$, $CHCl_2Br$, CH_2Br_2, $CH_2{=}CCl_2$, $CHCl{=}CCl_2$, C_3H_7Br, CH_2CH_2Br, $(CH_3)_2CHBr$, $(CH_3)_3CBr$, $BrCH_2CH_2Br$, $ClCH_2CH_2Cl$, and CH_3I in a 50 % propanol-2—water mixture result in the formation of complexes of the $Co^{III}TSP{-}R$ type, where R is an alkyl group from the corresponding halosubstituted derivative.

The successive debromination of bromoform resulting in the formation of CH_2Br_2 as the main product occurs both during noncatalytic photolysis and in the presence of TiO_2—CoTSP with silanized or nonmodified TiO_2. However, the reaction rate is significantly higher in the presence of the CoTSP complex. At ~20 °C and at concentrations of TiO_2—CoTSP of 1 mg L^{-1} and of bromoform of 34 mmol L^{-1}, the rates 20 min after the beginning of the reaction were 1.3, 2.8, and $14 \cdot 10^4$ mol min^{-1} for silanized, nonmodified, and modified TiO_2—CoTSP, respectively. Only traces of methane and bromomethane are present even after 8 h of the reaction.

The suggested reaction mechanism is similar to that described previously[41] for HDH of polychlorosubstituted derivatives of cyclopropane; the removal of the first bromine atom is presented in the scheme, and the other atoms are removed by repetition of the reaction cycle. As can be seen from this scheme, the solvent serves as a hydrogen donor:

$$TiO_2{-}Co^ITSP + CHBr_3 \longrightarrow TiO_2{-}CoTSP{-}CHBr_2 \xrightarrow{h\nu}$$

$$\longrightarrow \dot{C}HBr_2 + TiO_2{-}CoTSP,$$

$$\dot{C}HBr_2 + (CH_3)_2CHOH \longrightarrow CH_2Br_2 + (CH_3)_2C{=}O.$$

Ni^{II} ions can be catalysts of the homogeneous reduction of bromo- and chloroorganic compounds by anthracene radical anions[46] or by other organic radical anions,[47] and the catalytic effect increases for less reactive compounds. Chlorotoluene, bromopropane, bromo- and chlorobenzenes, 1-bromo-2-methyl-2-methoxycyclopropane, and 1,1-dichloro-2,2-diphenylcyclopropane were reduced in such reactions. The authors mention that under similar conditions Co^{II} ions can manifest both catalytic and inhibition effects.

2. Hydrodehalogenation of aryl halides

HDH of aryl halides occurs in the presence of heterogeneous and homogeneous metal-containing catalysts, in processes including phase-transfer catalysis.

2.1. Hydrodehalogenation in the presence of heterogeneous catalysts

Catalytic HDC of aryl halides is performed, as a rule, in the presence of metallic catalysts based on platinum or nickel group metals.

HDC of chlorobenzenes on the Pd/Al_2O_3 catalyst is described in Ref. 48. Chlorinated benzenes and phenols were hydrodechlorinated in the presence of 0.5 % Pd/Al_2O_3 reduced by hydrogen at 300 °C.[49] The relative reactivity depends on the position of the chlorine atom: if it is at the *ortho*-position to the OH group or to another chlorine atom, its elimination is difficult. Chlorine atoms at the *meta*- and *para*-positions are removed more easily. For example, HDC of 2,4-dichlorophenol gives only one product, 2-chlorophenol. The authors established the existence of two temperature regions of the reaction, and in the low-temperature region the existence of a substituent at the *ortho*-position to the chlorine atom sharply decreased the rate of HDC.

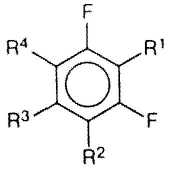
Vapor-phase HDC of chlorbenzene occurs in the presence of Pt/Al_2O_3 or Pt/H—BEA zeolite.[50] The initial activity of the zeolite-containing catalyst is high, however, coking and oligomerization cause its deactivation. The stability of the catalyst increases when the Brönsted acidic centers are replaced with Na^+ ions.

As in the case of alkyl halides, HDH is efficient in the presence of Pd/C at low temperatures (5—150 °C) and at pressures lower than 4 atm in the presence of acceptors of HHal such as alkaline metal hydroxides in alcohol solutions.[12]

Transition metals (Pd and Ni) on Sibunit and CFC carbon supports developed at the Institute of Catalysis of the Siberian Branch of the RAS cause successive HDC of 1,2,4,5-tetrachlorobenzene under relatively mild conditions (20—70 °C).[51] Complex hydrides were used as the hydrogen source. In the presence of one of the tested systems, 4 % $Pd/CFC—NaH(LiAlH_4)_{0.5}$, HDC occurs with the selective formation of 1,2,4-trichlorobenzene. Using several physicochemical methods, the authors showed that Pd particles more than 100 Å in size are inactive in HDC.

Reductive debromination of *p*-bromotoluene was studied in air in the presence of sodium borohydride and isopropanol. The reaction was catalyzed by rhodium and ruthenium complexes fixed on γ-aminopropyl-containing silica gel.[52] As should be expected, the activity and stability of almost all studied complexes in the reaction in air were lower than those for the reactions in hydrogen or in inert gas atmospheres. Only in the presence of immobilized ruthenium tetraacetate does the activity decrease less substantially (the initial reaction rates are 1.37 and 1.17 mol $(\text{min mol Ru})^{-1}$ in an argon atmosphere and in air, respectively); however, the activity of this catalyst is almost 6 times lower than that of the immobilized rhodium complex $[Rh_2(O_2CMe)_4]$, which is considerably less stable in air. The halogen is replaced, in the opinion of the authors, by hydrogen from the borohydride molecule, however, this conclusion seems insufficiently substantiated. In the earlier works of the same authors, the catalytic effect of complex catalysts in reactions of hydrogen transfer from alcohols[53] and, in particular, from the α-position of propanol-2,[54] to ketones was studied. As has been already mentioned, the mechanism of the replacement of halogen by a hydrogen of the solvent in the presence of rhodium triphenylphosphine complexes was substantiated in Ref. 37. A similar transfer can also occur in the reaction described in Ref. 52.

In a Hoehst Company patent, organic amines serve as hydrogen donors in the removal of halogen atoms (except fluorine) in halosubstituted 1,3-difluorobenzenes of general formula **A** (where $R^1—R^4$ = H, Cl, or Br, and more than one of the $R^1—R^4$ substituents is Cl or Br) under mild conditions (70—140 °C) in the presence of a palladium catalyst (Pd/C). For example, 2,4-difluorochlorobenzene is transformed into 1,3-difluorobenzene at 5—60 °C in the presence of tri-(*p*-dodecyl)amine, catalyst, and hydrogen.[55]



A

Both homogeneous and heterogenized rhodium(II) complexes can debrominate *para*-bromotoluene.[56]

Catalysts with a high content of nickel (30—70 %) on nickel aluminate with crystallites 50—150 Å in size exhibit high activity and selectivity (with minimum hydrogenation of the aromatic ring) in reductive dehalogenation, for example, in the dechlorination of chlorobenzene.[57]

The known method of dechlorination by zinc in an alcohol alkali[58] or by the nickel-zinc Urushibara catalyst[59,60] has been modified.[61] The reduction of aryl halides to arenes occurs efficiently in ethanol in the presence of zinc and catalytic amounts of nickel. For example, the conversion of iodobenzene to benzene is 92 % after 24 h at 60 °C in ethanol in a nitrogen atmosphere, while it is 98 % in dimethylformamide in a hydrogen atmosphere. It is significant that under these conditions halogen is replaced by hydrogen from the solvent according to the scheme:

$$NiBr_2 + Zn \longrightarrow Ni^0 + ZnBr_2, \tag{7}$$

$$Ni^0 + EtOH \longrightarrow HNi(OEt), \tag{8}$$

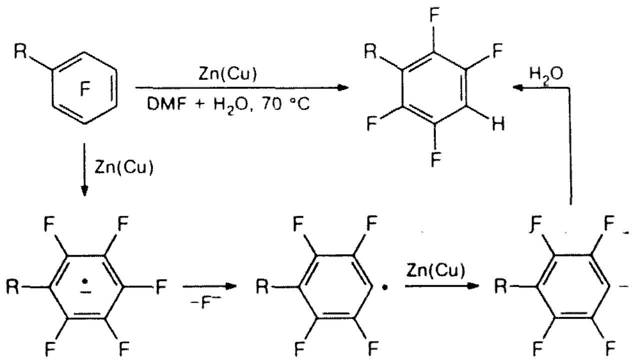
$$2HNi(OEt) + Zn \longrightarrow H_2 + 2Ni^0 + Zn(OEt)_2, \tag{9}$$

$$ArX + H_2 \xrightarrow{Ni^0} ArH + HX, \qquad (10)$$

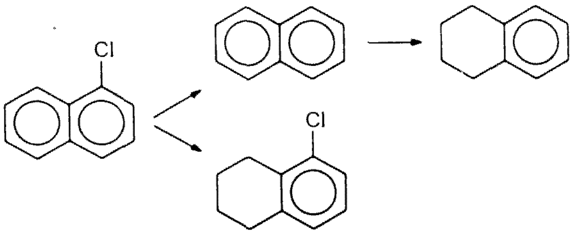
$$2HX + Zn(OEt)_2 \longrightarrow ZnX_2 + 2EtOH. \qquad (11)$$

The degrees of conversion of the other aryl halides after the same length of time (24—48 h) are the following: bromobenzene (36 h), 47 %; chlorobenzene (36 h, added H_2O), 72 %; and *p*-bromotoluene (48 h), 47 %.

Defluorination was unusually easily performed in Ref. 62. The partial defluorination of fluoroalkylbenzenes occurs under static conditions at low temperature (70 °C) in the presence of a zinc-copper catalyst in dimethylformamide. Compounds of general formula C_6F_5R (R = CF_3, $CF_2CF_2CF_3$) lose one fluorine atom in the benzene ring to form 4-H-C_6F_4R. The authors[62] suggest a radical ion mechanism of hydrodefluorination by the scheme:



Carbon black (BP-2000) accelerated HDH reactions of substituted polycyclic aromatic compounds in the presence of an organic hydrogen donor by 4 times and more.[63] Tetralin or 9,10-dihydrophenanthrene were used as hydrogen donors, and the reaction did not occur in their absence. At the ratio substrate : solvent : catalyst = 1 : 4 : 0.1 and temperature 410 °C, HDH of 9-bromophenanthrene (thermal conversion 20 %, catalytic conversion 46 %), and 1-bromo- and 1-chloronaphthalene (thermal conversion 17 and 13 %, catalytic conversion 64 and 50 %, respectively) occurred readily, and HDH of chlorobiphenyl occurred noticeably less easily (thermal and catalytic conversions were 2 and 5 %, respectively). The partial hydrogenation of the hydrocarbon fragment was observed in parallel with HDH, for example, by the reaction:



The selectivities of the reactions of thermal and catalytic dehalogenation of 1-bromo- and 1-chloronaphthalenes differ only slightly, which, in the authors' opinion, attests to the similarity of the mechanisms of thermal and catalytic reactions. The presented results are of practical significance, because condensed aromatic compounds model the reactivity of coals and petroleum residues under similar conditions.

High activity and selectivity in dehalogenation of chlorobenzene with minimum hydrogenation of the aromatic ring was manifested by a catalyst with a high content of nickel (30—70 %) with crystallites 50—150 Å in size and spinel-type nickel aluminate as the support.[57]

Haloaromatic compounds (halobenzenes, polychlorophenols) undergo HDH along with hydrogenation on a NiO—clay catalyst at 150—220 °C and 14—38 kPa.[64] For example, when a 30 % solution of hexachlorobenzene in methylene dichloride was conveyed to this catalyst (activated with hydrogen for 10 min at 200 °C) and was hydrogenated for 10 min at the same temperature, the conversion to cyclohexane was 100 %. Chlorobenzene and tetrachlorobenzene also form cyclohexane under the same conditions, while condensed compounds such as tetrachloronaphthalene and polychlorobiphenyls additionally undergo hydrogenolysis of the ring to form cyclohexane and methylcyclohexane. It is clear from the data presented that this nonselective process can be successfully used for treating toxic wastes.

Nickel-molybdenum catalysts are usually used for HDH of aryl chlorides. For example, in several works,[65,66] the catalytic HDH of 1,2,3-trichlorobenzene was studied using a Ni—Mo/Al_2O_3 catalyst in the presence of hydrogen at 200—350 °C with nonpolar solvents, decane or hexadecane, as the reaction medium. The obtained[65] time dependences of the concentrations of the products and reagent are very important, because polychlorobenzenes are used as models of various halogen-containing organic compounds that are industrial wastes.

Many chlorine-containing organic wastes contain sulfide admixtures. Several works have been devoted to the study of the effects of these admixtures on the catalysts and parameters of HDC reactions. For example, the authors of Ref. 67 studied the effect of sulfidization on HDC of *o*-dichlorobenzene in the gas phase at 300 °C and 2 MPa over reduced and sulfidized nickel, molybdenum, and nickel-molybdenum catalysts supported by aluminum oxide. The reaction occurs successively with the intermediate formation of chlorobenzene on all catalysts. Sulfidization affects the activity of catalysts in different ways. For Ni/Al_2O_3, Mo/Al_2O_3, and Ni—Mo/Al_2O_3, the relative activities of sulfidized and nonsulfidized forms are 0.3, 1.4, and 2.2, respectively. The selectivity with respect to chlorobenzene decreases after preliminary sulfidization. For example, the maximum conversion to chlorobenzene is 40 % for sulfidized and 17 % for nonsulfidized nickel-molybdenum catalysts.

The authors found positive synergism in the action of nickel and molybdenum in the nickel-molybdenum catalyst: the activity of the latter is threefold higher than the total activity of the separate nickel and molybdenum catalysts. This effect is not manifested in the reduced catalyst.

Changing the hydrogen pressure in the range from 3.5 to 10 MPa exerts almost no effect on the rate of dehalogenation of 1,2,3-trichlorobenzene in the presence of these catalysts.[66] Dehalogenation of 1,2- and 1,3-dichlorobenzenes on the nonsulfidized form of the catalyst occurs in parallel, and they react with hydrogen to form chlorobenzene and then benzene. The sulfidized catalyst leads, in addition, to hydrocracking of benzene. The authors believe that hydrogen undergoes dissociative Langmuir type adsorption, and the reaction on the surface is the rate-limiting stage.

2.2. Hydrodehalogenation in the presence of homogeneous catalysts

The homogeneous HDH of aryl chlorides has been recently performed using palladium complexes with chelated phosphine ligands in the presence of a base.[68]

$$\text{PhCl} \xrightarrow[\text{NaOH, CH}_3\text{OH}]{\text{Pd(OAc)}_2\text{ + 2dippp}} \text{PhH}$$

Only aryl bromides and iodides have been previously reduced by such complexes due to the great ease of oxidative addition of a metal to Ar—Br and Ar—I bonds.[69] The catalysts were prepared *in situ* in the reaction of $Pd(OAc)_2$ with two equivalents of dippp [dippp = 1,3-bis(diisopropylphosphino)propane]. Two reductive systems were used in the work: NaOH in methanol (1) and sodium formate in alcohol or dimethylformamide (2). Chlorobenzene is completely transformed to benzene after 20 h at 100 °C when NaOH : PhH = 2.

Selective HDH with other functional groups is possible in the presence of this reductive system, which is a substantial advantage over heterogeneous catalytic reduction.

Noble metal salts catalyze the cleavage of C—Hal bonds in aryl halides and the subsequent transfer of hydrogen from organic solvents.[70] Secondary cyclic amines are good donors of hydrogen, and methanol, in the authors' opinion,[70] serves as the best solvent. It is noteworthy that methanol as other aliphatic alcohols can participate in hydrogen transfer reactions as hydrogen donors.[71]

Another series of known dehalogenating agents, sodium borohydride and its derivatives, can also be modified by the addition of nickel salts.[72] Borohydride $[NaBH_2(OCH \cdot 2CH_2OCH_3)]_2$ obtained *in situ* in the reaction of $NaBH_4$ and 2-methoxyethane in THF is a strong dehalogenating agent and transforms γ-hexachlorocyclohexane to benzene at 68 °C after 0.5 h in 99 % yield and α-chlorotoluene to toluene after 2 h in 91 % yield. The addition of $NiCl_2$ results in a noticeable increase in the activity: γ-hexachlorocyclohexane is completely transformed into benzene after 15 min, and α-chlorotoluene is transformed into toluene after 1 h.

Simple Ni^{II} salts react with sodium borohydride to yield a black precipitate of "nickel boride" that is active in hydrogenation. By contrast, soluble compounds are formed in the reactions of nickel complexes of some porphyrins with $NaBH_4$. Such complexes,[73] exhibiting noticeable catalytic activity in HDC reactions of polyhalosubstituted derivatives of benzene and biphenyls, have been obtained. For example, 1-bromonaphthalene is transformed into naphthalene (99 %, 40 °C, 60 min), 2,6-dibromobiphenyl is transformed into biphenyl (100 %, 25 °C, 60 min), and 1,3- and 1,4-dibromobenzenes are transformed into benzene (40 °C, 40 min), in ethanol : acetonitrile mixtures in ratios of 2 : 1, 4 : 1, and 2 : 5, respectively. The degree of dechlorination of polychlorobenzenes is substantially lower. For example, the dechlorination (40 °C, 1.3 h, ethanol : acetonitrile = 6 : 1) of 1,2,3,4-tetrachlorobenzene results in the formation of a mixture of chlorobenzene (traces), dichlorobenzenes (15.2 % total), and 1,2,4- and 1,2,3-trichlorobenzenes (73 and 10 %, respectively). Approximately the same composition of products is obtained in the HDC of 1,2,4,5-tetrachlorobenzene. Chlorobenzene (7 to 8 %) is formed from 1,2,3- and 1,2,4-trichlorobenzenes at 30—45 °C; however, the total degree of dechlorination of 1,2,3-trichlorobenzene is higher: after 20 min of the reaction, the overall degree of transformation is 77 %, while it is only 47 % in the case of 1,2,4-trichlorobenzene. It is very probable that this difference is explained by the use of solvents with different polarity (in the first case, ethanol : water = 4 : 1, and in the second case, ethanol : acetonitrile = 4 : 1).

The authors suggest several proofs for the radical mechanism of hydrodechlorination. For example, it is shown by the H—D-exchange method that halogen is replaced by both the hydrogen atom of the CH group of ethanol and the hydride hydrogen atom from borohydride. The introduction of cumene, a good hydrogen donor, into the reaction mixture, strongly decreases the rate and degree of transformation, and bis-cumyl is present in the products. Therefore, the following sequence of elementary stages was suggested:

$$\text{LNi}^{\text{I}} + \text{RX} \longrightarrow \text{LNi}^{\text{II}} + \text{R}^{\cdot} + \text{X}^{-}, \qquad (12)$$

$$\text{LNi}^{\text{I}} + \text{RX} \longrightarrow \text{LNi}^{\text{II}} + \text{RX}^{-\cdot}, \qquad (13)$$

$$\text{RX}^{-\cdot} \longrightarrow \text{R}^{\cdot} + \text{X}^{-}, \qquad (14)$$

$$\text{R}^{\cdot} + \text{BH}_4^{-} \longrightarrow \text{RH} + \text{BH}_3^{-\cdot}, \qquad (15)$$

$$\text{LNi}^{\text{II}} + \text{BH}_4^{-} \longrightarrow \text{RH} + \text{LNi}^{\text{II}}\text{H} + [\text{BH}_3], \qquad (16)$$

$$\text{R}^{\cdot} + \text{LNi}^{\text{II}}\text{H} \longrightarrow \text{RH} + \text{LNi}^{\text{I}}, \qquad (17)$$

$$\text{R}^{\cdot} + \text{CH}_3\text{CH}_2\text{OH} \longrightarrow \text{RH} + \text{CH}_3\text{CH}^{\cdot}\text{OH}, \qquad (18)$$

$$\text{R}^{\cdot} + \text{C}_6\text{H}_5\text{CH(CH}_3)_2 \longrightarrow \text{RH} + \text{C}_6\text{H}_5\text{C}^{\cdot}(\text{CH}_3)_2, \qquad (19)$$

and the cumyl radical rapidly dimerizes to form biscumyl.

According to this mechanism, high selectivity is achieved for the reduction of substrates with nonequivalent halogen atoms, which depends on stage (14), dissociation of the radical anion.

A bifunctional homogeneous rhodium catalyst obtained from $[(Me_5C_5)RhCl_2]_2$ reduced in the presence of isopropanol and excess triethylamine was used for reductive dechlorination of substituted chlorobenzenes and hydrogenation of double bonds.[74] Excess base is needed to neutralize the HCl formed in the reactions:

$$C_6H_5Cl + H_2 \longrightarrow C_6H_6 + HCl,$$

$$C_6H_6 + 3H_2 \longrightarrow C_6H_{12},$$

$$HCl + NEt_3 \longrightarrow [HNEt_3]Cl,$$

$$[HNEt_3]Cl + NaOH \longrightarrow Et_3N + NaCl + H_2O.$$

The reaction was performed in a steel autoclave under hydrogen pressure at 75 °C. Under these conditions, first chlorobenzene, then 1,2,4-trichlorobenzene and 1-chloronaphthalene consecutively split off chlorine atoms and only then are hydrogenated. For example, 60 min after the beginning of the experiment, chlorobenzene forms a mixture of 14.4 % benzene and 17.9 % cyclohexane, and in 240 min 100 % cyclohexane is formed. Similarly, after 60 min of HDC of 1,2,4-trichlorbenzene, the reaction mixture contains 12 % dichlorobenzene and 1 % chlorobenzene, and after 360 min, it contains 100 % cyclohexane. Completely deuterated benzene is formed as an intermediate in the HDC of completely deuterated chlorobenzene. Therefore, the gas phase hydrogen does not participate in HDC. The dechlorination rate is almost independent of the amount of triethylamine; hence, the authors believe that its only role is to bind HCl. The data presented make it possible to conclude that the solvent is a hydrogen donor in this reaction as well.[74]

The reductive dechlorination of chlorophenols by vitamin B_{12} is described in Ref. 75.

2.3. Hydrodehalogenation under conditions of phase-transfer catalysis

Fast and efficient replacement of halogen by hydrogen is possible under phase-transfer catalysis conditions. For example, fast reactions of triethylammonium ethoxide with polychloroalkanes in ethanol at −20 °C with formation of chloroalkanes have been described.[76] The fast replacement of halogen by hydrogen in polyhalobenzenes,[77] *o*-, *m*-, and *p*-bromotoluenes, and 2-chloro-*m*-xylenes[78] occurs in the presence of a multiphase system consisting of a hydrocarbon solvent, a solution of a strong alkali, quaternary onium salt, and a Pt/C catalyst. 1,2,4,5-Tetrachlorobenzene reduces to benzene after 30 min at 50 °C at the molar ratio Pd : Cl = 1 : 130. In the authors' opinion, the onium salt forms the third liquid phase on the catalyst surface, the reaction occurs in this phase, and the halosubstituted derivatives are distributed between the hydrocarbon phase and the phase of the interphase carrier. The addition of inorganic salts, especially with bulky ligands (I^-), decreases the rate and selectivity of hydrodehalogenation, because the inorganic anions occupy the sites of the substrate molecules in the adsorption layer.

The reduction rates of the three isomeric chlorotoluenes differ both in the presence and in the absence of onium salts. For some alkylbenzenes, the change in the rate in the presence of onium salts is especially substantial. Isomeric chloroethylbenzenes can be reduced 50 times more rapidly in the presence of Aliquat 336. This method makes it possible to reduce 2-chlorotoluene, which is very difficult to reduce by other methods. However, in some cases (for example, in a nonpolar solvent), the presence of an onium salt can decrease the reaction rate.

The presence of onium salts can also change the selectivity of the reduction of isomeric aryl halides: in the presence of Aliquat 336 in diethyl ether at 20 °C, *p*-dichlorobenzene reacts five times more slowly than the *o*-isomer, while in the absence of the onium salt, the rates of their reduction are equal.[78] The most interesting case is the reduction of a mixture of polychlorobiphenyls (Arochlor 1254) to biphenyl in 99 % yield (H_2, isooctane, 50 °C, 3 h) performed by the same authors. In this case, the degree of transformation was only 54 % for the same time in the absence of the onium salt.

The same system with the addition of sodium hypophosphite as a hydrogen source was used for HDC of 1,2,4,5-tetrachlorobenzene.[79] The dechlorination occurs sequentially to form 1,2,4-trichlorobenzene, a mixture of *o*-, *m*-, and *p*-dichlorobenzenes, chlorobenzene, and benzene. In the presence of Pd/C, a 50 % aqueous solution of KOH, Aliquat 336 as a phase-transfer catalyst (PTC), and sodium hypophosphite (molar ratio tetrachlorobenzene : Pd : $NaH_2PO_4 \cdot H_2O$: PTC = 1 : 0.03 : 2.8 : 0.4) at 50 °C, tetrachlorobenzene disappears from the reaction mixture after 2 h of the reaction, and almost quantitative transformation to benzene occurs after 2.5 h. Under similar conditions, after 20 min of the reaction the degrees of transformation of chloro- and bromobenzene to benzene were 97 and 100 %, and those of *p*-chloro- and *p*-bromoanisole to anisole were 90 and 100 %, respectively.

For monohalobenzenes, the rate of halogen replacement decreases in the normal order: I > Br > Cl > F. It is noteworthy that the maximum rate of dechlorination of tetrachlorobenzene occurs when methanol and isooctane are used as solvents, however, the solubility of the substrate in methanol is very low, and, in addition, nonpolar solvents increase the degree of dechlorination. The authors do not understand the reasons for this phenomenon. They believe that in the presence of carbon-supported palladium, HDC occurs *via* the dissociative adsorption of molecules on the surface followed by the addition of hydrogen,[80] because this explanation accounts for the important role of surface phenomena. In addition, the substantial effect of KOH can be explained within the framework of this mechanism: the HCl formed blocks the catalyst surface, but cannot rapidly be removed in the presence of a strong base, and the phase-transfer catalysts promote this process by transporting hydroxide anions from the aqueous phase to the catalyst surface. The Langmuir dependences of the kinetic constants on the amount of the onium salt prove that onium salts are also adsorbed on the catalyst surface.[78]

An efficient method for reduction of aryl chlorides using a two-phase system in the presence of a phase-transfer catalyst and Rh^{III} complex has been described.[81]

Thus, many catalysts containing group VIII metals are active in HDC of halogen-containing aromatic compounds, and the halogen atoms can be replaced by hydrogen atoms originated either from the gas phase or from an organic donor.

3. Hydrodechlorination of halosubstituted derivatives of dioxines, polychlorobiphenyls, and halogen-containing industrial wastes

Many of the studies of HDC considered in the previous section, for example, HDC of polychlorinated benzenes, were carried out to model reactions that occur during HDC of more complex molecules, including polychlorinated dibenzofurans, dibenzodioxines, *etc.*, since multicomponent mixtures of similar products of variable composition exist under real conditions. Therefore, here we present only data obtained using polychlorinated biphenyls (PCBP), polychlorodioxines, and real industrial wastes. As a rule, PCBP are deactivated in industry by burning, including burning in plasma when dioxines can be present in the burning products, or by oxidation or reduction in the presence of alkali, which usually requires an inert atmosphere. Therefore, the development and utilization of catalytic methods for decomposing PCBP are very urgent problems. The methods described below using complex hydrides in the presence of nickel compounds are similar to catalytic methods.

A reductive system containing derivatives of sodium borohydride along with nickel salts was used for HDC of both haloaromatic derivatives[72] and a mixture of polychlorobiphenyls (Arochlor 1016).[82] Sodium borohydride and lithium aluminum hydride are not very active in dehalogenation of haloaromatic hydrocarbons, but can reduce nickel to Ni^0 when its salts are added to the reaction system. Thus, metallic nickel *in statu nascendi* is in fact the catalyst. The 100 % dechlorination of tetrachlorobiphenyl to biphenyl occurs with the reductive system $NaBH_2(OCH_2CH_2OCH_3)_2$: $NiCl_2$: THF (6 : 2.5 : 70) at 68 °C after 1.5 h. The same system at the ratio of reagents (6 : 0.75 : 20) is active in the dechlorination of Arochlor 1016; however, the degree of dechlorination is lower in this case. After 36 h the conversion of the initial mixture is 90 %, and the reaction products contain 3.2 % mono- and 3.1 % dichlorobiphenyls along with biphenyl. The authors mention that the catalytic system is deactivated during HDC.

Several individual polychlorinated biphenyls have been hydrochlorinated by sodium borohydride in the presence of the nickel catalyst[83] using a method similar to that described in Ref. 72. However, in this case, Raney nickel or a homogeneous triphenylphosphine complex of Ni^0 was used instead of a nickel salt as the nickel catalyst. The reaction nearly does not occur in the absence of nickel compounds, while in the presence of nickel, HDC occurs rather intensely at low temperatures. A high selectivity of substitution of the chlorine atom at a certain position (2-, 3-, 4-) is observed only in the presence of the nickel complex. In the authors' opinion, the selectivity-determining stage is the oxidative addition of aryl halide to the catalyst, the Ni^0 complex.

The addition of a catalyst substantially improves the parameters of electro- or photochemical HDC. For example, the quantum yield of the products of the photochemical dechlorination of mono- and polychlorinated biphenyls in an acetonitrile—water mixture (9 : 1) increases by several orders of magnitude in the presence of sodium borohydride.[84] It is significant that the degree of increase in the quantum yield is higher for the compounds that are the most difficult to reduce (for example, in the presence of $NaBH_4$, the quantum yield of products of HDC of 3,5-dichlorobiphenyl increases 240 times, that of 3,5,3′,5′-tetrachlorobiphenyl 170 times, and that of 2,4,2′,4′-tetrachlorobiphenyl only 2.3 times). It is more important that the strong increase in the rate occurs simultaneously with an increase in selectivity of HDC up to the complete suppression of the formation of byproducts (they can include highly toxic chlorinated dibenzofurans and hydroxychlorobiphenyls as well as polymerization products). Thus, the addition of $NaBH_4$ as a catalyst makes it possible to overcome the main disadvantage of photolytic reactions, their low selectivity.

In the presence of a microemulsion containing didodecyldimethylammonium bromide, dodecane, and water (21 : 57 : 22 wt. %), zinc phthalocyanine and the tetrasodium salt of phthalocyaninetetrasulfonic acid, the parameters of the electrochemical reduction of PCBP on a lead cathode improve noticeably.[85] The degrees of dechlorination of Arochlor 1221, 1232, and 1260 were close to 100 % after 10, 12, and 18 h of electrolysis, respectively. The authors believe that this method will efficiently decompose PCBP in real industrial waste.

Both nickel and palladium catalysts (4 % Pd/C, 8 % Ni/C) as well as a broader range of metal hydrides as hydrogen sources (NaH, MgH_2, $LiAlH_4$, $NaBH_4$, $NaH(LiAlH_4)_{1/2}$) were used for the low-temperature HDC.[86] The most active catalyst in this HDC was the system containing palladium (4 % Pd/C—$NaH(LiAlH_4)_{1/2}$), where fibrous carbon material was used as a support. At 70 °C, this system efficiently promotes HDC of chlorobenzene, 1,2,4,5-tetrachlorobenzene, hexachlorobenzene, and 2,3-dichlorodibenzo-*p*-dioxin (DBD). As usual, the reaction occurs sequentially. For example, in the case of DBD, first monochlorodibenzo-*p*-dioxin is formed and then dibenzo-

p-dioxin. The use of several physicochemical methods made it possible to establish the formation of complex palladium hydrides on the support surface.

In the presence of organic amines and the complex catalyst Cp_2TiBH_4 (formed *in situ* from dichlorotitanocene Cp_2TiCl_2 and $NaBH_4$), PCBP is efficiently hydrodechlorinated. The reaction mixture contains 80 % dichlorobiphenyl after 12 min of the reduction of Arochlor 1248 at 125 °C, while complete HDC to biphenyl occurs after 24 h. The authors suggested the reduction mechanism including the one-electron transfer from the titanium complex with organic amine formed during the reaction to the polychlorobiphenyl molecule.[87]

Metallic iron serves as a catalyst in HDC of Arochlor 1221 when it is heated above 300 °C.[88] For example, at 300 °C after 1 h, the degree of conversion is 78 %, while at 400 °C at the same conversion the degree of dechlorination increases (biphenyl comprises up to 95 % of the catalyzate). Both the yield of biphenyl and the degree of conversion decrease dramatically at 500 °C. When CH_2Cl_2 is added to the reaction mixture, the degree of HDC remains almost unchanged, and it increases slightly when water is added. In the presence of D_2O, the biphenyl formed contains deuterium. In the authors' opinion, both organic admixtures and water can be hydrogen donors. However, the data presented on H—D exchange are not quantitative, which makes it impossible to estimate the contribution of direct H—D exchange, which can be rather substantial at the reaction temperatures.

The active catalyst of HDC of polychlorinated biphenyls (Arochlor 1260 or 1254) is obtained by the modification of metallic iron with metallic Pd (0.05 wt. %).[89] In the presence of a 1 : 3 : 1 methanol : water : acetone solution, the complete conversion of the initial mixture occurs after 5 to 10 min. Increasing the amount of the catalyst and the content of Pd results in an increase in the reaction rate, while increasing the concentration of methanol results in a decrease in the reaction rate. Biphenyl was the sole product. The authors believe that the replacement of chlorine occurs on the catalyst surface and involves hydrogen formed due to the corrosion of Fe in water *via* the reaction:

$$Fe^0 + 2\,H_2O \longrightarrow 2\,Fe^{2+} + H_2 + 2\,OH^-,$$

however, no detailed study of the reaction mechanism was performed in this work. Nevertheless, this method is very promising for the purification of sewage.

4. Hydrodechlorination of organic compounds containing various functional groups

Many works have been devoted to HDC of compounds, including heterocyclic compounds, containing other functional groups. In this review, we consider the results of the study of HDH in the presence of mainly nitrogen-containing functional groups, predominantly nitro groups, because these works, which often use electrochemical data, are significant for understanding the mechanisms of catalytic HDH.

The previously mentioned homogeneous HDC of aryl chlorides using palladium complexes with chelate phosphine ligands in the presence of a base[68] is also appropriate for selective HDC in the presence of other functional groups. As can be seen from Table 3, even groups sensitive toward bases, such as CHO and CN, are retained under the reaction conditions in the presence of system (2) (sodium formate in alcohol or dimethylformamide). Electron-releasing substituents decrease the reaction rate, which indicates that oxidative addition is the rate-determining stage.

The opposite sequence of the reduction of halonitrobenzenes is observed in the presence of palladium complexes immobilized on γ-aminopropyl-containing silica gel and promoted with KOH, when isopropanol is used as the hydrogen source.[90] The replacement of chlorine and bromine in the corresponding halonitrobenzenes begins only after the complete (*m*- and *p*-chloronitrobenzene) or partial (35 % for *o*-chloronitrobenzene) reduction of the nitro group, and the rate of its reduction is much lower than that of nonsubstituted nitrobenzene. In the latter case, the dechlorination rate increases 5 times after completion of the reduction of the nitro group. The authors[90] believe that halonitrobenzenes coordinate at their nitro group more strongly with the complex catalyst. In fact, in the reduction of the nitrobenzene—*p*-bromotoluene mixture, the rate of nitrobenzene reduction remains unchanged, and the rate of hydrodebromination of *p*-bromotoluene decreases by 30 times. The rate of the replacement of bromine dramatically increases after the completion of the hydrogenation of nitrobenzene.

Both dehalogenation and reduction of the nitro group can occur in the electrocatalytic or catalytic reduction of 2-iodonitrobenzene in the presence of Raney alloys acting as a cathode or a catalyst. A comparison of the distribution of the products in the reduction of 2-iodonitrobenzene under electrochemical and catalytic conditions using Raney nickel and cobalt in an aqueous-methanol (93 : 7 by weight) medium[91] shows substantial differences: nitrobenzene, the main product of catalytic reduction in the presence of KOH, is not observed on the cyclic voltammetric curve. The main products obtained in the catalytic hydrogenation of 1-iodonitro-

Table 3. Effect of the nature of the substituent on the degree of transformation of *para*-substituted chlorobenzenes in the presence of palladium complex catalyst $[Pd(OAc)_2 + 2dippp]$ and sodium formate[68]

$p\text{-X—C}_6H_4Cl \longrightarrow \text{X—Ph}$

X	*T*/°C	Conversion to X—Ph (%)
H	100	90
CHO	100	100
CN	100	100
NO_2	100	70
CH_3CO	100	87
CH_3	100	14
CH_3	150	100
CH_3O	100	11
CH_3O	150	100
NH_2	100	15

Table 4. Catalytic hydrogenation of 2-iodonitrobenzene (10^{-2} mol) on electrodes of Raney-type metals in a methanol-aqueous mixture (93 : 7 wt. %)[91]

No	Catalyst	pH	Hydrogenation products (%)				Conversion (%)
			$PhNH_2$	$PhNO_2$	$2-IC_6H_4NHOH$	$2-IC_6H_4NH_2$	
1	Ni	13	98	2	0	0	100
2		7	71	0	1	28	95
3		10	17	3	13	67	81
4		3	40	1	8	49	92
5	Co	13	7	86	0	7	58
6		7	10	4	29	57	21
7		10	3	0	0	97	20
8		3	5	19	0	76	18
9	Cu	13	18	69	0	13	75
10		7	10	25	30	35	20
11		10	0	16	34	50	6
12		3	12	12	38	38	9

benzene (10^{-2} mol L^{-1}) on electrodes of the corresponding Raney-type metal are listed in Table 4.

The distribution of products in a strongly alkaline medium (dehalogenated products predominate) shows that on nonpoisoned catalysts the rate constant of deiodination is substantially higher than that of the reduction of the nitro group. Therefore, $PhNH_2$ is mainly obtained by hydrogenolysis of the C—I bond followed by the hydrogenation of nitrobenzene. On less active cobalt and copper catalysts, the second stage (hydrogenation) is so slow that nitrobenzene is the main product. The same is observed in less basic media in the presence of a pyridine or acetate buffer, when the catalysts are poisoned with products of dehalogenation or due to the adsorption of acetic acid.

Thus, comparing the relative amounts of halogenated and nonhalogenated products of the catalytic hydrogenation of 2-iodonitrobenzene, the authors find many general features with electroreduction on a mercury electrode, when the electron transfer mechanism is preferable.

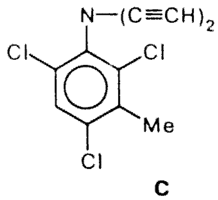
Recently,[92] HDC of substituted chlorobenzenes RC_6H_4Cl (where R = NH_2, OH, CH_3, Cl, CF_3, or H) was performed using 10 % $Ni/\gamma—Al_2O_3$ at 523 K. The hydrodechlorination rate is almost independent of the spatial arrangement of the substituents, but it strongly increases as the donor properties of the substituents increase in the order chlorotrimethylbenzene < dichlorobenzene < chlorotoluenes < chlorophenols < chloroaniline. The analysis of the Hammett equation for the HDH reactions allowed the authors to assume the electrophilic mechanism of the reaction.

Photoelectrochemical dehalogenation of *p*-halonitrobenzenes was carried out in Ref. 93. The authors uphold the viewpoint that the mechanisms of dehalogenation of alkyl and aryl halides substantially differ. Alkyl halides are characterized by one-electron reduction followed by fast cleavage of the *C*-halogen bond; aryl halides are characterized by a consecutive mechanism, in which radical anions of different stabilities are formed. It has been established that electrochemical reduction can induce insignificant dehalogenation of *p*-iodonitrobenzene, while the combined action of photo- and electrochemical reduction results in the efficient removal of both bromine and chlorine in the corresponding *p*-halonitrobenzenes even at room temperature. Therefore, the photochemical activation of radical anion intermediates by light with wavelengths between 300 and 600 nm strongly affects the reaction route, and the dehalogenation rates for bromo- and chloronitrobenzenes depend in different ways on the frequency of the radiation used. For example, in the case of *p*-chloronitrobenzene, shorter-wave radiation is more efficient because the C—Cl bond is more stable than the C—Br bond. The authors present a probable explanation for the fast occurrence of the reaction *via* a low-energy excited state in *p*-bromonitrobenzene.

Absorption of long-wave irradiation can be designated as a $\pi^*—\pi^*$-transition, in which the transition state has a doublet character. By contrast, irradiation with short-wave light (330 nm) causes the excitation of π-electrons, which results in a quadruplet transition state. In the latter case, excess halogen ions are forbidden according to the spin conservation rule.

In alcohols or aqueous media in the presence of a palladium catalyst in a hydrogen atmosphere, HDH of 2-amino-5-halopyridines forms 2,3-diaminopyridines. For example, 2-amino-5-bromo-3-nitro-4-methylpyridine gives 78 % 2,3-diamino-4-methylpyridine after 50 min in the presence of Pd/C and methanol at 23—50 °C.[94] It has been previously established[95] that only the chlorine atom can be selectively removed in the hydrogenation of 2-methyl-3-nitro-4-methoxymethyl-5-cyano-6-chloropyridine on a palladium-modified chloromethylated styrene—divinylbenzene copolymer under mild conditions (45—55 °C) in alcohols or water.

The selective removal of only chlorine from the *para*-position is observed in the reduction of acetylenide (C) in the presence of Pd/C, sodium formate, and CH_3CN. The yield of $3-Me-2,6-(Cl)_2C_6H_2NH_2$ is as high as 90 %.[96]



C

Several halosubstituted benzoic acids, phenols, anilines, and nitrogen-containing heterocyclic compounds are quantitatively dehalogenated by sodium borohydride in an aqueous-alkaline medium in the presence of catalytic amounts of a palladium salt,[97] evidently under the catalytic effect of palladium formed *in situ*. The effects of substituents in the *ortho*-position are noted.

* * *

Looking at the data on the possible mechanisms of hydrodehalogenation, the following generalizations should be mentioned. The majority of the authors conclude that anion or radical anion intermediates are necessary for HDH, while under radical conditions HDH is accompanied by the complete or partial destruction of the hydrocarbon framework of molecules. In many cases, studies of the reaction mechanisms are difficult due to the mobility of linear molecules, because of which isotopic and other methods do not give results as reliable as those obtained in studies of molecules with more rigidly fixed structures. For example, the sequential HDH of 3,3,7,7-tetrachlorotricyclo[4.1.0.$0^{2,4}$]heptane in the presence of many metal-containing homogeneous and heterogeneous catalysts made it possible to reliably substantiate the ionic mechanism of the reaction, involving the transfer of a hydride ion from the α-alkyl group of the alcohol used as a solvent.[41,60] The results presented in this review testify that similar ionic mechanisms occur in most cases of selective catalytic hydrodehalogenation.

The considerable advances in biological and related enzymatic methods of HDH help the study of the mechanisms of catalytic HDH; however, the low rates of these reactions provide no grounds so far for optimism concerning industrial application. Therefore, metal-containing heterogeneous catalysts are presently the most efficient, and by modifying them it is possible to achieve the desired changes in the selectivity and activity of HDH reactions.

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References

1. A. R. Pinder, *Synthesis*, 1980, 425.
2. I. A. Cusumano, *in TOCAT 2. (Second Tokyo Conf. on Advanced Catalytic Science and Technology)*, Aug. 21–26 (1994), Progr.—Abstr., 403.
3. J. R. Shoebrecht and F. Janssens, Eur. Pat. 570,050, *Chem. Abstr.*, 1994, **120**, 106376.
4. T. Suzuki and S. Kawahara, JP 04,364,136, *Chem. Abstr.*,1992, **118**, 254378.
5. E. I. Gelperin, Yu. M. Bakshi, J. V. Tarasova, A. K. Avetisov, R. Touride, O. Finlayson, and M. Tiernan, *Proc. II Conf. "Modern Trends in Chemical Kinetics and Catalysis,"* Part II(1), November 21–24, 1995, Novosibirsk, Russia, 218.
6. S. Morikawa, S. Samejima, M. Yoshitake, S. Tatematsu, JP 04-26636, *Chem. Abstr.*, 1990, **116**, 255162.
7. G. S. Dasaeva, S. M. Velichko, Yu. A. Treger, and I. I. Moiseev, *Kinet. Katal.*, 1990, **31**, 858 [*Kinet. Catal.*, 1990, **31** (Engl. Transl.)].
8. L. J. Matheson and P. G. Tratnyek, *Environ. Sci. Technol.*, 1994, **28**, 2045.
9. O. A. Zaidman, E. I. Verkhutova, L. N. Zanaveskin, and Yu. A. Treger, *Khim. Prom-st* [*Chemical Industry*], 1991, 515 (in Russian).
10. C. D. Schreier and M. Reinhard, *Chemosphere*, 1995, **31**, 3475.
11. E. D. Boyes, D. R. Coulson, G. W. Coulston, M. P. Diebold, P. L. Gai, G. A. Jones, C. S. Kellner, J. J. Leron, and L. E. Manzer, *Prepr.—Am. Chem. Soc., Div. Pet. Chem.*, 1993, 38 (4), 847, *Chem. Abstr.*, 1994, **120**, 220759.
12. I. Pri-Bar, D. Azoulay, and O. Buchman, Eur. Pat. 456,879, *Chem. Abstr.*, 1990, **116**, 112944.
13. S. Morikawa, S. Sameijima, M. Yositake, and S. Tatematsu, JP 04-29941, *Chem. Abstr.*, 1990, **116**, 255164.
14. N. Takada, T. Moruta, and H. Ooshio, JP 04-13638, *Chem. Abstr.*, 1990, **116**, 193698.
15. W. Dafinger and L. Schmidhammer, Eur. Pat. 523,553, *Chem. Abstr.*, 1993, **118**, 236 409.
16. R. Ohnishi, W. L. Wang, and M. Ishikawa, *Appl. Catal.* A, 1994, **113**, 29.
17. R. M. Jansen, Eur. Pat. 571,920, *Chem. Abstr.*, 1994, **120**, 133827.
18. C. J. Shields and G. Goodyear, PCT Int. Appl. WO 94 02439, *Chem. Abstr.*, 1994, **120**, 191107.
19. H. Aoyama, E. Seki, and S. Koyama, PCT Int. Appl. WO 93 16023, *Chem. Abstr.*, 1994, **120**, 54176.
20. S. Morikawa, M. Yoshitake, and S. Tatematsu, JP 05-17379, *Chem. Abstr.*,1992, **118**, 254379.
21. R. Ohnishi, H. Suzuki, W. Wang, and M. Ishikawa, *Sekubai* (*Catalyst*), 1991, **33**, 91.
22. J. Takita, H. Yamada, Y. Mizuhara, and T. Ishihara, *Chem. Express*, 1990, **5**, 785.
23. Y. Takita, H. Yamada, T. Ishihara, and Y. Mizuhara, *J. Chem. Soc. Japan, Chem. Ind. Chem.*, 1991, **5**, 584.
24. T. Mori, W. Ueda, and Y. Morikawa, *TOCAT 2 (Second Tokyo Conf. on Advanced Catalytic Science and Technology)* Aug. 21–26 (1994), Progr.—Abstr., 403.
25. N. N. Kuznetsova, E. S. Lokteva, V. *V.* Lunin, and S. L. Yudina, *Kinet. Katal.*, 1995, **36**, 131 [*Kinet. Catal.*, 1995, **36** (Engl. Transl.)].
26. J. M. Cognion and D. Guillet, Eur. Pat. 506525, *Chem. Abstr.*, 1991, **117**, 233429.
27. J. Koppe, K. Kraenke, D. Schoenfeld, and H. Haugk, Ger. Pat. DE 4200790, *Chem. Abstr.*, 1994, **120**, 61641.
28. F. Zaera and S. Tjandra, *J. Phys. Chem.*, 1994, **98**, 3044.
29. K. Ogura, J. Guo, and Y. Jun, *Huanjing Huauue*, 1993, **12**, 66, *Chem. Abstr.*, 1993, **119**, 54985.
30. S. Okazaki and H. Habutsu, *J. Fluorine Chem.*, 1992, **57**, 191.
31. Y. Morikawa, T. Ikawa, and W. Ueda, JP 04-120032, *Chem. Abstr.*, 1991, **117**, 111129.
32. Y. Morikawa, T. Ikawa, W. Ueda, JP 04-120031, *Chem. Abstr.* 1991, **117**, 111128.
33. A. Stüre, J. Grub, and M. Lux, Pat. BRD 40120074, 1990.
34. J. Mochida, Y. Kojima, H. Tejima, and M. Morita, JP 05-271123, *Chem. Abstr.*, 1994, **120**, 133826.
35. T. Yoshida, T. Honda, and K. Nakagawa, JP 03-264542, *Chem. Abstr.*, 1990, **116**, 173551.
36. R. B. Timmons, W. L. Jang, Y. He, and D. J. Houpt, US Pat. 5,276,240, *Chem. Abstr.*, 1994, **120**, 216696.
37. E. S. Lokteva, V. V. Lunin, A. N. Kovredov, and L. I. Zakharkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 539 [*Bull. Acad. Sci.*, 1989, **38**, 473 (Engl. Transl.)].
38. C. B. Castro, M. C. Helvenston, and N. O. Belser, *Environ. Toxicol. Chem.*, 1994, **13**, 249.

39. T. Arai, K. Kashitani, H. Kondo, and S. Sasaki, *Bull. Chem. Soc. Japan*, 1994, **67**, 705.
40. C. J. Gantzer and L. R. Wackett, *Environ Sci. Technol.*, 1991, **25**, 715.
41. V. V. Lunin and E. S. Lokteva, *Kinet. Katal.*, 1989, **30**, 674 [*Kinet. Catal.*, 1989, **30** (Engl. Transl)].
42. R. G. Harrison and T. G. Richmond, *J. Am. Chem. Soc.*, 1993, **115**, 5303.
43. S. Li and L. R. Wackett, *Biochemistry*, 1993, **32**, 9355.
44. U. E. Krone, R. K. Thauer, and H. R. C. Hogenkamp, *Biochemistry*, 1989, **28**, 4908.
45. R. J. Kuhler, G. Santo, T. R. Candill, E. A. Betterton, and R. G. Arnold, *Environ. Sci. Technol.*, 1993, **27**, 2104.
46. V. V. Yanilkin, N. I. Maksimyuk, and Yu. M. Kargin, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1022 [*Russ. Chem. Bull.*, **43**, 957 (Engl. Transl.)].
47. V. V. Yanilkin, N. I. Maksimyuk, E. I. Gritsenko, and Yu. M. Kargin, *Izv. Akad. Nauk, Ser. Khim.*, 1991, 261 [*Russ. Chem. Bull.*, 1991, **40**, 241 (Engl. Transl.)].
48. A. G. Anshits, A. R. Suzdorf, S. I. Tsiganova, and N. N. Anshits, *EuroCat-1 (1st Eur. Congr. Catal., Montpellier, Sept. 12—17 1993)*, Book Abstr., **2**, 1993, 926.
49. A. R. Suzdorf, S. I. Tsyganova, N. N. Anshits, S. *V.* Morozov, and A. G. Anshits, *Sib. Khim. Zh.* [*Siberian Chem. J.*], 1992, No. 6, 131 (in Russian).
50. E. J. Greyghton, M. H. W. Burgers, J. C. Jansen, and H. van Bekkum, *Appl. Catal., A: Gen.*, 1995, **128**, 275.
51. V. I. Simagina, I. *V.* Stojanova, V. M. Mastikhin, E. M. Moroz, V. A. Yakovlev, and V. A. Likholobov, *Proc. II Conference "Modern Trends in Chemical Kinetics and Catalysis,"* Part II(2), November 21—24, 1995, Novosibirsk, Russia, 361.
52. V. N. Isaeva, Ya. *V.* Smirnova, and V. Z. Sharf, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 613 [*Russ. Chem. Bull.*, 1993, **42**, 582 (Engl. Transl.)].
53. V. Z. Sharf, L. Kh. Freidlin, and V. N. Krutii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 735 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **26** (Engl. Transl.)].
54. V. Z. Sharf, L. Kh. Freidlin, I. S. Shekoyan, V. N. Krutii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 834 [*Bull. Acad. Sci., Div. Chem. Sci.*, 1977, **26**, no. 4 (Engl. Transl.)].
55. T. Schach and T. Papenfuhs, Eur. Pat. 598,338, *Chem. Abstr.*, 1995, **121**, 108188.
56. V. Z. Sharf and V. I. Isaeva, *Stud. Surf. Sci. Catal.*, 1993, **75**, 2281.
57. W. Fahruschon, P. Kripylo, J. Koppe, and M. Wilde, Ger. Offen, DE. 4-230553, *Chem. Abstr.*, 1995, **121**, 159725.
58. H. Yamanaka, R. Oshima, K. Teramura, and T. Ando, *J. Org. Chem.*, 1972, **37**, 1734.
59. K. Isogai and T. Kazama, *Nippon Kagaku Zassi. J. Chem. Soc. Japan*, 1967, **88**, 106.
60. E. S. Lokteva, T. E. Klimova, V. V. Lunin, *Vestn. Mosk. Un-ta, Ser. 2, Khim.* [*Bull. Moscow Univ., Ser. 2, Chem.*], 1986, **27**, 587 (in Russian).
61. M. Sakai, M. Lee, K. Yamaguchi, Y. Kawai, K. Sasaki, and Y. Sakakibara, *Bull. Chem. Soc. Japan*, 1992, **65**, 1739.
62. V. I. Krasnov and V. E. Platonov, *Zh. Org. Khim.*, 1993, **29**, 107 [*J. Org. Chem.*, 1993, **29** (Engl. Transl.)].
63. M. Farfcasiu, S. C. Petrosius, and E. P. Ladner, *J. Catal.*, 1994, **146**, 313.
64. M. Moeder, D. Bender, and G. Reinhardt, Ger. (East) DD 294965, *Chem. Abstr.*, 1990, **116**, 151297.
65. F. Giola, V. Famiglietti, and F. Murena, *J. Hazard. Mater.*, 1993, **33**, 63.
66. F. Giola, V. Famiglietti, and F. Murena, *J. Hazard. Mater.*, 1994, **38**, 277.
67. M. Novak and M. Zdrazil, *Bull. Soc. Chim. Belg.*, 1993, **102**, 271.
68. Y. Ben-David, M. Gozin, M. Portnoy, and D. Milshtein, *J. Mol. Catal.*, 1992, **73**, 173.
69. R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, London, 1985, 461.
70. H. Imai, T. Nishiguchi, M. Tanaka, and K. Fucuzumi, *J. Org. Chem*, 1977, **42**, 2309.
71. Y. Sasson and J. Blum, *J. Org. Chem.*, 1975, **40**, 1887.
72. S. M. H. Tabaei and C. U. I. Pittman, *Hazard. Waste Hazard. Mater.*, 1993, **10**, 431.
73. M. Stiles, *J. Org. Chem.*, 1994, **59**, 5381.
74. D. T. Ferrughelli and J. T. Horvath, *J. Chem. Soc. Chem. Communs.*, 1992, 806.
75. M. H. Smith, *From Diss. Abstr. Int. B*, 1994, **54 (9)**, 4586, *Chem. Abstr.*, 1994, **120**, 265678.
76. G. A. Tolstikov and S. S. Savanov, *Proc. II Conference "Modern Trends in Chemical Kinetics and Catalysis,"* Part I, November 21—24, 1995, Novosibirsk, Russia, 44.
77. C. A. Marques, M. Selva, and P. Tundo, *J. Org. Chem.*, 1993, **58**, 5256.
78. C. A. Marques, M. Selva, and P. Tundo, *J. Org. Chem.*, 1994, **59**, 3830.
79. C. A. Marques, M. Selva, and P. Tundo, *J. Chem. Soc. Perkin Trans., I.*, 1993, 529.
80. I. Pri-Bar and O. Buchman, *J. Org. Chem.*, 1986, **51**, 734.
81. V. V. Grushin and H. Alper, *Organometallics*, 1991, 1620.
82. S. M. H. Tabaei, C. U. I. Pittman, and K. T. Mead, *J. Org. Chem.*, 1992, **57**, 6669.
83. J. A. Roth, S. R. Dakoji, R. E. R. C. Hughes, and R. E. Carmody, *Environ. Sci. Technol.*, 1994, **28**, 80.
84. G. A. Elping, E. M. Florio, A. J. Bourque, X.-H. Quan, and J. D. Stuart, *Environ. Sci. Technol.*, 1988, **22**, 952.
85. S. Zhang and J. Rusling, *Environ. Sci. Technol.*, 1993, **27**, 1375.
86. V. A. Simagina, I. V. Stojanova, V. V. Litvak, V. M. Mastikhin, V. A. Jakovlev, and V. A. Likholobov, in *EUROPACAT-II (II Eur. Congr. Catal., Maastricht, Sept. 3—8, 1993), Book of Abstracts*, 329.
87. Y. Liu, J. Schwartz, and C. L. Cavallaro, *Environ. Sci. Technol.*, 1993, **27**, 1375.
88. F.-W. Chuang, R. A. Larson, and M. S. Wessman, *Environ. Sci. Technol.*, 1995, **29**, 2460.
89. C. Grittini, M. Malkomson, Q. Fernando, and N. Corte, *Environ. Sci. Technol.*, 1995, **29**, 2898.
90. V. Z. Sharf, V. F. Dovganyuk, V. I. Isaeva, and B. I. Maksimov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 534 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 468 (Engl. Transl.)].
91. B. J. Cote, D. Despres, R. Labrecque, J. Lamothe, J. M. Chapuzet, and J. Lessard, *J. Electroanal. Chem.*, 1993, **355**, 219.
92. R. G. Compton, R. A. W. Dryfe, and A. C. Fisher, *J. Electroanal. Chem.*, 1993, **361**, 275.
93. A. R. Suzdorf, S. *V.* Morozov, A. M. Covalev, and A. G. Anshits, *in: EUROPACAT-II, (2 Eur. Congr. Catal., Maastricht, Sept. 3—8 1993) Book of Abstracts*, 337.
94. K. Hirata and H. Kaai, JP 05-339236, *Chem. Abstr.*, 1994, **120**, 244702.
95. M. V. Klyuev, A. A. Nazivilin, and N. V. Sidorova, *Author's Certificate* 1643535 USSR, *Byul. Izobret.* [*Bull. Invent.*], 1991, 1986 (in Russian).
96. R. G. Pews, J. E. Hunter, and R. M. Wehmeyer, *Tetrahedron*, 1993, **49**, 4809.
97. D. V. Davydov and I. P. Beletskaya, *Metalloorg. Khim.*, 1993, **3**, 111 [*Organomet. Chem. USSR*, 1993, **3** (Engl. Transl.)].

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