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Prospects for the development of methods for the processing of organohalogen waste. Characteristic features of the catalytic hydrogenolysis of halogen-containing compounds

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Abstract. Comparative characteristics of methods for the processing and detoxification of organohalogen waste are described. It is shown that the catalytic hydrogenolysis method is the most promising. Numerous catalytic systems used for hydrogenolysis are examined, the influence of the dispersity of the catalysts on their activity is discussed, and data concerning the kinetics and mechanisms of these reactions as well as the possible elementary reactions occurring on the catalyst surface are analysed. Also discussed are the factors determining the reactivity of the C–Hal bonds in the hydrogenolytic reactions. The bibliography includes 159 references.

I. Introduction

One of the most acute problems in the creation and organisation of low-waste ecologically safe industries producing organohalogen compounds involves the processing and detoxification of the waste. An unpleasant feature of this waste is that in almost all cases they are xenobiotics, i.e. products which have no analogues in nature, and there are no natural means of combating them. On the other hand, not all the procedures for the conversion of organohalogen compounds can be used for their utilisation and detoxification. The severe ecological and economic limitations imposed on modern industries producing organohalogen substances give rise to a series of requirements as regards procedures for the treatment of waste from these industries. Such requirements include the renewability of the carbon-containing raw materials or a high commercial value of the products formed, the economic viability of the treatment, a high degree of conversion, the universality of the procedure, and the lack of toxic substances among the products. The prospects for the development of methods for the processing of organohalogen waste should be considered in the light of these requirements.

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II. Comparative characteristics of the methods for the processing and detoxification of organohalogen waste

A large proportion of the existing methods for the processing and detoxification of waste from industries producing halogen-containing substances have to some extent exhausted their possibilities. In particular, the disruptive effect of tetrachloromethane on the Earth's ozone layer, discovered in recent years,[1,2] gives rise to the problem of gradually winding-down the output of industrial chlorolysis, which is a source of this product together with tetrachloroethene. This requirement of the Montreal Protocol[3,4] is not excessive, since the existing industrial capacity greatly exceeds the need for tetrachloroethene,[2,5,6] while better technologies have been developed for alternative industrial processes for the production of this substance.[5,7]

The method for the detoxification of organohalogen waste with the aid of thermal combustion is also unsuitable nowadays, since it leads to the formation of highly toxic products such as chlorine, nitrogen oxides, phosgene, and dioxins.[1,8–11] Furthermore, thermal combustion requires a large consumption of fuel and gives rise to the irreversible loss of the hydrocarbon raw material, the evolution of carbon dioxide into the environment, and rapid wear of the equipment. The effectiveness of the method for the detoxification of toxic waste in dilute gases is low.[1,8–12]

The catalytic combustion method is free from the majority of the above deficiencies.[5,8,12,13] However, despite the notable progress in the development of new catalytic systems for the combustion of organohalogen waste, the range of substances susceptible to detoxification remains comparatively narrow.[8,14] Evidently this method cannot be regarded as promising, since the irreversible loss of raw material resulting from its application does not conform to the concept of low-waste technologies.

The gas-phase thermal and catalytic dehydrochlorination processes are more attractive[1,5,8,15–17] because they lead to the possibility of the transformation of organohalogen waste into useful products. However, the range of practical applications of these methods is significantly limited, which is associated either with the lack of demand for the dehydrochlorination products or with the impossibility of achieving the process in principle. In particular, chloromethanes, chlorobenzenes, and chlorobiphenyls cannot serve as the dehydrochlorination objects.

Hydrodehalogenation or hydrogenolysis may be regarded as the most universal and promising method for the treatment and detoxification of organohalogen waste.[1,2,6,9–12,18–56] Together with ecological safety, it ensures in many instances the regeneration of the initial raw material, which may open a path to the

creation of low-waste technologies.† The regeneration of the raw material from the waste in the industrial production of vinyl chloride and chlorobenzene can serve as an example,[55,57,58] chlorobenzene itself being regenerated in the latter case.[23,57-59] In certain cases, hydrogenolysis leads to the formation of useful products which can be used in related industries. Thus the organochlorine waste from the industrial production of *sym*-tetrachloroethane and vinyl chloride based on ethyne may be subjected to thermal hydrogenolysis with formation of gaseous ethyne, ethene, and hydrogen chloride.[38] After the absorption of the latter, the hydrogenolysis gases can be combined with the pyrolysis ethyne and directed to the stage in which pure ethyne is isolated. If catalytic hydrogenolysis is used in the treatment designed for the preferential formation of ethane, then the hydrogenolysis gases formed can be directed, after the absorption of hydrogen chloride from them, to the natural gas line, which proceeds to the stage in which pyrolysis ethyne is obtained. Finally, when the hydrocarbons formed as a result of hydrogenolysis cannot be returned to the technological cycle, their employment as a fuel is most rational.[10] The likely usefulness of hydrogenolysis as a detoxification method is emphasised by the recently published data concerning the conversion of polychlorodibenzodioxins, polychlorodibenzofurans, and polychlorobiphenyls into ecologically safe products.[60]

As regards hydrogen chloride, there are two possibilities for its utilisation. The first consists in the preparation of nongaseous hydrochloric acid. This procedure is effective in the exhaustive hydrogenolysis of C_1-C_4 organochlorine compounds, since gaseous organic products sparingly soluble in water are formed, which guarantees a high quality of the acid obtained. The second possibility presupposes the use of hydrogen chloride as the reactant in hydroxychlorination and hydrochlorination processes. This variant is more suitable for hydrogenolytic processes in which liquid organic products are formed: in this case, the hydrochloric acid formed on absorption of gases is contaminated by organic impurities and there is no commercial demand for it. An example of the use of recovered hydrogen chloride as the reactant is provided by the hydroxychlorination of benzene to chlorobenzene.[16]

The Exxon Company has proposed a very interesting procedure for the utilisation of the hydrogen chloride obtained in the hydrogenolysis of chlorobenzenes: the hydrogen chloride is extracted from the reaction products treating them with triethylamine[61] and the resulting salt $[HN(C_2H_5)_3]Cl$ is treated with aqueous alkali:

$$[HN(C_2H_5)_3]Cl + NaOH \longrightarrow N(C_2H_5)_3 + H_2O + NaCl.$$

This regenerates triethylamine, which is returned to the technological cycle. Evidently this version of the binding of hydrogen chloride is most effective if the production of organochlorine substances is combined with the production of chlorine and sodium hydroxide in which sodium chloride serves as the raw material.

The principal advantage of the hydrogenolytic processes is the possibility of a flexible selection of the optimum type of treatment of the waste by varying the process parameters, the catalytic or initiating system, the reaction medium, and the hydrogen donors. The practical use of hydrogenolysis for the treatment of waste is not restricted to halogen-containing compounds and this method has been tested successfully on nitrogen-, sulfur-, and oxygen-containing compounds,[15,44,45,62-74] including the processes for the detoxification of sulfur and nitrogen oxides and CO.[75,76] The importance of the hydrogenolytic processes for the detoxification of organoelement compounds, the combustion of which leads to the formation of a series of many highly toxic products, such as Cl_2, Br_2, sulfur and nitrogen oxides, dioxins, etc., giving rise to new acute ecological problems, must be specially emphasised.

Apart from hydrocarbons, the hydrogenolysis products include hydrogen compounds of the halogens, sulfur, and nitrogen, having distinctly acid or basic properties, which facilitates their extraction by sorption methods. The universality of hydrogenolysis as a method for the detoxification of waste has been confirmed by its effectiveness in the removal of organoelement impurities from waste water and technological gases.[32,40,75,77-80]

On the other hand, certain hydrogenolytic processes are of independent importance as a method of synthesis of valuable products on an industrial or preparative scale. This applies to the preparation of fluorohydrocarbons by the hydrogenolysis of the corresponding chlorofluorohydrocarbons[22,36,48] and of nitrobenzenes from chloronitrobenzenes,[81] the synthesis of substituted anilines,[82] the conversion of aliphatic esters into higher alcohols,[83-87] and the synthesis of sterically strained amines,[88] purine,[49] and other preparations.[51,52,89,90]

There has been an extremely interesting communication about the use of hydrogenolysis for the isolation of pure *m*-xylene from a mixture of *m*- and *p*-xylenes.[25] The mixture is monochlorinated, which affords a 90% yield of 2-chloro- and 4-chloro-xylenes. The latter are readily separated by distillation and are subjected to further gas-phase hydrogenolysis on a platinum catalyst deposited on activated carbon.

Finally the possibility of converting freons into ecologically safe commercial products[4,91-95] is of fundamental importance for the solution of the global problem of the protection of the Earth's ozone layer.

III. Hydrogenolytic methods. Prospects for their development

Hydrogenolysis may be achieved by thermal, catalytic, and reagent procedures. This classification is to some extent arbitrary because it does not reflect the entire wide variety of the reactions underlying these processes. In particular, it is to be expected that the mechanism of the catalytic action of metals differs fundamentally from the mechanism of enzymic hydrogenolysis[97,98] and that the metals themselves can perform various catalytic functions depending on the type of the hydrogenolytic agent. Evidently the effect of the majority of metals on gas-phase hydrogenolytic reactions involving molecular hydrogen is determined by homolytic processes on the surface,[30,35,98-105] whereas the liquid-phase catalytic reactions occurring on treatment with alcohols and with formic acid and its salts[106-108] involve the transfer of a hydride anion. Published data concerning the possibility of inducing catalytic reactions involving the hydrogenolysis of organohalogen compounds by microwave radiation[109] constitute yet another piece of evidence for the multiplicity of these processes. In this case, the catalyst (iron oxide) accumulates the radiation energy and transfers it to the chemisorbed molecule of the organohalogen compound. The latter undergoes homolytic decomposition at the C–Cl bond and initiates the radical hydrogenolytic process. The methods involving the electrochemical reduction and reductive coupling of organohalogen compounds[110-114] may be classified as reagent methods subject only to certain stipulations.

Among the numerous hydrogenolytic methods, the catalytic and thermal methods are of practical interest. The reagent methods, involving the use of expensive hydrogen donors such as Na + ROH, $LiAlH_4$, Ar_3SnH,[25,115-117] $NaBH_4$,[63,118-121] hydrazine,[80] Zn + protic acid,[122] and finely dispersed zinc,[123] are only of preparative importance.

In the present review, attention is concentrated on the catalytic hydrogenolytic reactions of organohalogen compounds, which are of greatest practical importance and have been comparatively little investigated. The data on the hydrogenolysis of organoelement compounds are used only to reveal the general characteristic features of this group of processes.

† In the large-scale industrial production of organochlorine substances, the creation of autonomous treatment plant is economically justified, as has been done by the Union Carbide Company, which has announced the organisation of the treatment of waste from the production of vinyl chloride with a potential output of 10 000 tonnes annually.[40]

IV. Catalytic systems for hydrogenolysis. The kinetics and mechanisms of the reactions

Numerous versions of catalytic hydrogenolysis have been described in the literature. The processes are carried out in both liquid and gas phases. The choice of catalytic systems is fairly wide. The vast majority of the reactions take place on Group IB, VB, VIB, VIIB, and VIII metals, including Pt, Pd, Rh, Ru, Ir, Os, Ni, Co, Fe, Re, Mn, Mo, W, Cr, V, Cu, Ag, and Au.

The properties of metallic catalysts, namely their activity, selective action, useful lifetime, etc. can be modified by fusion with other metals, by the introduction of promoting additives, and by varying the carrier. Catalytic systems based on the Rh–Ir,[124] Cu–Rh,[18] Co–Mo,[44] Ni–W,[45] Ni–Mo,[45,125–128] Pd–Pt, Pd–Ga, Pd–Al, Pd–Ru,[101] Pd–Sn, Pd–Pb, Pd–Ge, Pd–K, Pd–Fe, Pd–Co, and Pd–Ag[93,100,129] bimetallic alloys have been proposed. Pd, Pt, Ru, Ir, Fe, Co, Ni, Cu, Cd, Ag, Au, V, Cr, Mo, W, Bi, Al, Hg, In, Sn, Te, Si, P, As, and Sb,[19,24,92,101,130] aluminium, boron, and titanium salts and oxides,[24] phosphines and phosphates,[5,130] alkali and alkaline earth metal hydroxides and oxides,[24,29,127] and phosphonium halides[31] are used as promoting additives to metallic catalysts. The range of carriers for metallic catalysts is fairly wide, including activated carbon,[80,93,130–139] diatomites,[18] aluminium oxide[125–129,135,136] chromium oxide,[135] silicon oxide,[9,12,26,39,99,134] iron oxide,[135] aluminosilicates,[24] calcium carbonate,[35] zeolites,[43,96] and barium sulfate.[52]

Copper,[23,29] palladium,[137,138] ruthenium, platinum, and rhodium[138,139] salts, chromium, iron, aluminium, nickel, and molybdenum oxides,[60,95,96,140] silicon oxide,[9,12,26,39,99] phosphine complexes of ruthenium rhodium, and iron,[91,106,108] and transition metal coenzymes, namely vitamin B_{12} (Co), the coenzyme F_{430} (Ni), and hematin (Fe)[97] merit attention among other occasionally employed catalytic systems. Vitamin B_{12} is used successfully for the treatment of organochlorine waste ($C_2H_3Cl_3$, $C_6H_6Cl_6$, $C_6H_3Cl_3$, C_6Cl_6, and C_2Cl_4), F_{430} is employed for the hydrodehalogenation of $C_6H_5CH_2Cl$, *o*-$ClC_6H_4CH_2Cl$, $C_6H_5CH_2CH_2Br$, and *p*-BrC_6H_4Br to $C_6H_5CH_3$, *o*-$ClC_6H_4CH_3$, $C_6H_5CH_3$, $C_6H_5CH_2CH_3$, and C_6H_5Br respectively by formate anions, and hematin is used in the utilisation of organoelement waste such as tetrachloromethane, hexachloromethane, *cis*- and *trans*-dichloroethenes, etc.

The theoretical principles underlying the catalytic hydrogenolysis of organohalogen compounds have been investigated inadequately, while kinetic data are scattered and contradictory. The region in which the reactions occur has been reported only in rare investigations, which to a large extent vitiates the kinetic data obtained and casts doubt on the catalytic activity[62,99,141] and substrate reactivity[30,136] series quoted in the literature. We may note that in those studies where the region in which catalytic hydrogenolysis on metals was subjected to a detailed analysis it was not possible to obtain the kinetic region. Thus the radioisotope label method showed that, in the temperature range 193–448 K, the true picture of the chemical interaction on the surface is distorted by adsorption and diffusion factors.[142] Kinetic analysis of the hydrogenolysis of chlorobenzene and 1,2-dichlorobenzene on Ni–Mo/γ-Al_2O_3 at 275–376 °C indicates that the rate of reaction is limited by adsorption and desorption processes.

Certain investigations were devoted to the solution of practical problems — the search for formal mathematical models of the processes.[60,143] However, such models, which are useful for the design of reaction apparatus and the optimisation of process conditions, yield little evidence for the interpretation of the mechanism of the catalytic hydrogenolysis.

Together with the temperature variations of the rates of hydrogenolysis of ethane, methylamine, and chloromethane, the structures and dispersities of the catalyst have been investigated.[62,98,141] This made it possible to give the reaction rates and the pre-exponential factors for a single surface metal atom — the catalyst active centre. The variations in catalytic activity in the Re–Os–Ir–Pt–Au and Ru–Rh–Pd–Ag series are attributed by the authors to the unequal capacities of ethane, methylamine, and chloromethane for sorption via the C–C, C–N, and C–Cl bonds on the surfaces of these metals.

However, the results obtained are to a large extent vitiated by the arbitrary assumptions adopted by the authors. In particular, one cannot neglect the relation between the activity of a single surface metal atom and the dispersity of the catalyst: it is well known that hydrogenolysis belongs to the class of structure-sensitive reactions, a characteristic feature of which is the dependence of the specific activity on the structure of the reaction centre.[145] The available data indicate a significant influence of the dispersity of the metallic catalysts on their activity in hydrogenolytic reactions.[65,102,129,145,146]

It is hardly correct to determine the activity of the catalysts of the hydrogenolysis of methylamine from the rates of formation of methane and ammonia,[62] since the authors themselves showed that at least one other side product — $(CH_3)_2NH$, $(CH_3)_3N$, $(CH_3CH_2)_2NH$, or CH_3CN — is formed to an appreciable extent on the majority of the catalysts which they employed (Ru, Pd, Rh, Ag, Re, Os, Pt, Ir, Au). Since the contributions of the main and side reactions depend on temperature, the attempt to determine the activation parameters does not yield reliable results and the observed isokinetic relation between the rates of these reactions cannot serve as an argument in support of a common mechanism of the hydrogenolysis of ethylamine and the side reactions complicating it on different catalytic systems.

Finally, the determination of the activities of the catalysts in the hydrogenolytic reactions of all the compounds investigated, carried out under the conditions of constant partial pressures of the substrate and hydrogen, is based on the doubtful *a priori* hypothesis that the reaction orders with respect to the reactants are equal on each catalyst. Furthermore, the presence of extrema in the catalytic activities presented above may serve as an indication that the rate-limiting stage of the process may also vary as a function of the adsorption capacity of the reactant. For a low adsorption capacity, the rate of reaction may be determined by the adsorption stage, but the greater the strength of the bonds between the chemisorbed species and the surface, the higher the rate of this stage. At the same time, the subsequent interaction of the reacting species on the surface becomes increasingly more difficult and in the limiting case it can become the stage which determines the overall rate of reaction.

The observed dependences of the reactivities of the metals on their positions in the Periodic Table can be explained also by the fact that the most favourable geometrical correspondence between the length of the chemisorption bond and the size of the unit cell of the catalyst crystal lattice is obtained in the region of the extremum.[147] This point of view, based on the multiplet theory of catalysis,[148] is confirmed by the dominant contribution of the entropy factor to the change in the specific activity of single atoms on passing from one metal to another.

The contradictory nature of the data on the kinetics of hydrogenolysis and on the catalytic activity series reflects, in our view, the complexity of the test systems due to the specificity of each catalytic system and the variations in the influence of various factors on the chemical processes occurring. The proposed reaction mechanisms are therefore valid only in specific cases and cannot be extended to other objects of hydrogenolysis. Nevertheless, from a formal point of view, the hydrogenolysis mechanisms discussed in the literature may be divided into two groups. The first group of mechanisms presupposes the adsorption of the components of the reacting systems on the catalytic surface, the interaction of the adsorbed species, and the subsequent desorption of the products from the surface (the Langmuir–Hinshelwood mechanism).[65,93,126] This approach has been used to interpret data on the kinetics of the hydrogenolysis of *p*-chloronitrobenzene to *p*-chloroaniline on ruthenium and platinum catalysts.[65,101] A characteristic feature of the proposed mechanism is the continued adsorption of hydrogen on the catalytic surface after it has been saturated by the organic

reactant. According to the authors, the physical preconditions for this to occur are the presence of free sites on the surface owing to the strong dipole–dipole repulsion of the polar nitro-groups of the adsorbed substrate and the small size of the hydrogen molecules. A similar mechanism has been proposed for the hydrogenolysis of tetrachloromethane on the Pt/η-Al_2O_3 catalyst.[35] The observed zero order of the reaction with respect to CCl_4 and the 0.5 order with respect to H_2 was justified by the authors in terms of the following scheme:

$$[H_2]_{ads} \rightleftharpoons [H^{\cdot}]_{ads} + [H^{\cdot}]_{ads}, \quad (1)$$

$$[CCl_4]_{ads} \rightleftharpoons CCl_3^{\cdot}(gas) + [Cl^{\cdot}]_{ads}, \quad (2)$$

$$CCl_3^{\cdot}(gas) + H_2(gas) \overset{fast}{\rightleftharpoons} CCl_3H(gas) + H^{\cdot}(gas), \quad (3)$$

$$CCl_3^{\cdot}(gas) + H^{\cdot}(gas) \xrightarrow{fast} CCl_3H(gas). \quad (4)$$

This scheme presupposes the preferential adsorption of CCl_4 on the catalyst surface:

$$CCl_4(gas) \overset{Pt}{\rightleftharpoons} [CCl_4]_{ads}. \quad (5)$$

The slight increase in the reaction orders with respect to the reactants as the temperature increases may indicate that the kinetics of the process follow the Langmuir–Hinshelwood mechanism.

Similar kinetic data have been obtained also in a study of the hydrochlorination of *cis*- and *trans*-dichloroethenes on Pt/Al_2O_3.[136] Although in view of the complexity of the systems investigated the authors themselves refrained from interpreting their data, one may suppose that the observed reaction orders with respect to the dichloroethenes indicate the adsorption saturation of the catalytic surface by the dichloroethenes and that the reaction order of 0.5 with respect to hydrogen corresponds to the dissociative nature of its adsorption.

The second group of mechanisms of catalytic hydrogenolysis is formally based on the analogy of this process with the selective oxidation reactions of hydrocarbons[149] and presupposes the alternate chlorination and reduction of the catalyst, which functions as a hydrogen and chlorine transferring agent between the reactans and the products.[99,129] This approach is based on the mechanism, proposed for the hydrogenolytic reactions of chlorobenzene on palladium–rhodium and palladium–tin alloy catalysts, which includes the following stages:

$$Pd{-}H + C_6H_5Cl(gas) \xrightarrow{k_1} Pd{-}Cl + C_6H_6, \quad (6)$$

$$Pd{-}H + HCl(gas) \xrightarrow{k_2} Pd{-}Cl + H_2, \quad (7)$$

$$Pd{-}Cl + H_2(gas) \xrightarrow{k_H} Pd{-}H + HCl. \quad (8)$$

The proposed mechanism is vulnerable to criticism. Firstly, the use in it of the method of stationary concentrations leads to the kinetic equation

$$r = \frac{k_1 k_H P_{C_6H_5Cl} P_{H_2}}{k_H P_{H_2} + k_1 P_{C_6H_5Cl} + k_2 P_{HCl}}, \quad (9)$$

where $P_{C_6H_5Cl}$, P_{H_2}, and P_{HCl} are the current partial pressures of chlorobenzene, hydrogen, and hydrogen chloride respectively. The equation differs from the experimental equation

$$r = \frac{k_1 k_H P_{C_6H_5Cl} P_{H_2}^{0.5}}{k_H P_{H_2}^{0.5} + k_1 P_{C_6H_5Cl} + k_2 P_{HCl}}, \quad (10)$$

indicating a different dependence of the rate of reaction on the partial pressure of hydrogen. Secondly, the observed constants

$$k_2 > k_1 \gg k_H,$$

which follow from the mechanism proposed by the authors, are inconsistent with the available thermochemical data. Thus one should expect that the entropies of activation for reactions (6) and (7) are similar and that the difference between the constants k_1 and k_2 should be determined solely by the difference between the bond dissociation energies $D(C_6H_5{-}H) - D(C_6H_5{-}Cl) = 15.3$ kcal mol^{-1} and $D(H{-}H) - D(H{-}Cl) = 1$ kcal mol^{-1}.[150] This difference between the dissociation energies should lead to the inequality $k_1 \gg k_2$, which conflicts with estimates by other workers.[99,129]

We believe that the kinetic data on the catalytic hydrogenolysis of chlorobenzenes presented above may be interpreted successfully within the framework of the Langmuir–Hinshelwood model. In this case, the parameters k_H, k_1, and k_2 of Eqn (10) reflect the adsorption capacity of the components. Indeed, the high value of k_2 is inconsistent with the high polarity of hydrogen chloride and its ability to form hydrogen bonds. On the other hand, the observed dependence of the reaction rate on the partial pressure of hydrogen reflects the dissociative character of its adsorption on platinum group metals, which has been confirmed by numerous experimental data.[144,151]

Analysis of the kinetic data shows that they can be usually described within the framework of the Langmuir–Hinshelwood model. The conclusion concerning the dissociative character of the adsorption of hydrogen on the metal surfaces, which follows from the proportionality of the rate of the reaction (or the numerator in the kinetic equation) to $P_H^{0.5}$, is of fundamental importance. The relatively low activation energies for the overall catalytic hydrogenolytic processes (Table 1) is an additional argument in support of the dissociative adsorption of hydrogen.

Table 1. The activation energies (E/kcal mol^{-1}) for the hydrogenolytic reactions.

Reaction	Catalyst	E	Ref.
$CH_3Cl + H_2 \longrightarrow CH_4 + HCl$	Ti film	16.1	102
$CH_2Cl_2 + H_2 \longrightarrow CH_3Cl + HCl$	Ti film	13.4	102
$CH_2Cl_2 + 2H_2 \longrightarrow CH_4 + 2HCl$	Ti film	13.3	102
$(CH_3)_3CCl + H_2 \longrightarrow (CH_3)_3CH + HCl$	Pt film	19.0	104
$(CH_3)_3CCl + H_2 \longrightarrow (CH_3)_3CH + HCl$	Pd film	18.0	104
$C_6H_5Cl + H_2 \longrightarrow C_6H_6 + HCl$	Pd/Al_2O_3	25.0	129
$ClHC{=}CHCl + H_2 \longrightarrow H_2C{=}CHCl + HCl$	Pt/Al_2O_3	27.5	136
$CH_3CH_2F + H_2 \longrightarrow C_2H_6 + HF$	Pd/C	12.0	30
$CH_3CHF_2 + 2H_2 \longrightarrow C_2H_6 + 2HF$	Pd/C	26.0	30
$CH_3CF_3 + 3H_2 \longrightarrow C_2H_6 + 3HF$	Pd/C	26.0	30

The fruitfulness of the Langmuir–Hinshelwood model is confirmed by the fact that it makes it possible to predict the inhibiting effects of the reactants and reaction products on the process and to estimate the adsorption capacities of the components. The lack of sensitivity of the hydrogenolytic reactions to the presence of acid active centres in the catalyst is apparently associated with the high adsorption capacity of hydrogen chloride: the adsorbed hydrogen chloride molecules themselves function as such centres and the contribution of the natural active centres of the catalyst to its catalytic activity becomes negligible. This may account for the failure of our attempts to modify the hydrogenolysis catalysts with alkaline reagents.

The elucidation of the nature of the elementary stages in the hydrogenolysis of halohydrocarbons is assisted by analysis of the composition of the products and by special studies of the mechanisms of these reactions. Evidently the substitution of the halogen by hydrogen requires the preliminary dissociation of carbon–halogen bonds. The preferential dissociation of these particular bonds is due to thermodynamic factors, which follow from the comparatively low C–Hal bond energies[150] and high metal–Hal bond energies. This is in fact the driving force of the chemisorption of halohydrocarbons. The nature of the dissocia-

tion of the C–Cl bonds on the catalytic surface has been investigated in a study[102] devoted to the hydrogenolysis of chloromethane and dichloroethane on titanium, palladium, and other metallic films. The use of the ^{13}C and ^{35}Cl isotopes made it possible to establish that the dissociation of the C–Cl bonds is irreversible. It was shown in the same study that the rate of deuterium exchange involving chloroalkanes is negligible compared with the rate of hydrogenolysis. A similar result had been obtained earlier in a study of the hydrogenolysis of chloroethane, bromoethane, and *tert*-butyl chloride on sputtered platinum and palladium films.[103, 104] The composition of the products formed in the hydrogenolysis of halohydrocarbons shows that the dissociation of the C–Cl bonds is not accompanied by the synchronous attack on the latter by an adsorbed hydrogen atom or another surface intermediate and is an independent elementary stage leading to the formation of surface radicals. The latter, which are kinetically independent species, are involved in further interactions, affording various products depending on the conditions and the type of catalytic system. This is confirmed by the formation of polymerisation products together with the products of the direct substitution of the halogen by hydrogen.

The following types of interactions involving the surface radicals formed as a result of the primary dissociation of the carbon–halogen bonds are possible.

1. Radical recombination reactions. The possibility of these interactions is confirmed by the formation of hexachloroethane as one of the products of the hydrogenolysis of tetrachloromethane on nickel–zeolite catalysts and Pd–Pt, Pd–Ga, Pd–Al, and Pd–Ru metallic alloy membranes.[43, 101] Tetrafluoroethene is also formed in the hydrogenolysis of difluoromethane on deposited Pd–Fe and Pd–Co catalysts.[93] We regard the appearance as a result of the hydrogenolysis of products containing twice the number of carbon atoms compared with the initial organic reactant as a result of the recombination of surface radicals. The observed discrepancy between the degrees of substitution of the carbon atoms in the primary fragments formed and in the recombination products is a consequence of the conversion of the primary fragments into new surface radicals with the same number of carbon atoms. Thus the formation of 1,1,1,2-tetrachloroethane as the product of the hydrogenolysis of tetrachloromethane on Ni–zeolite catalysts[43] should be regarded as the result of the recombination of the surface radicals $[CCl_3^{\cdot}]_{ads}$ and $[CH_2Cl^{\cdot}]_{ads}$, the latter being the product of the conversion of the $[CCl_3^{\cdot}]_{ads}$ radical.

2. Reactions involving the elimination of chlorine radical species. One of the variants of the conversion of the surface radical $[CCl_3^{\cdot}]_{ads}$ into the radical $[CH_2Cl^{\cdot}]_{ads}$ may involve preliminary dechlorination with elimination of a chlorine radical species, i.e.

$$[CCl_3^{\cdot}]_{ads} \underset{-Cl^{\cdot}}{\rightleftharpoons} [CCl_2]_{ads} \underset{-Cl^{\cdot}}{\rightleftharpoons} [CCl^{\cdot}]_{ads},$$

and the subsequent interaction of the adsorbed fragment with hydrogen. This view, put forward by Mishchenko and Senina,[100] makes it possible to account for the formation of appreciable amounts of methane even at low degrees of conversion under the conditions of the hydrogenolysis of tetrachloromethane. Methane is formed as the dominant substitution product also in the hydrogenolysis of difluoromethane.[93] Unique data have been obtained in a study[43] where it was shown that the hydrogenolysis of tetrachloromethane on Pt/η-Al_2O_3 leads to the exclusive formation of chloroform and methane with a constant ratio $[CHCl_3]/[CH_4]$ over the entire range of degrees of conversion. This result apparently reflects the specificity of the catalytic system employed by the authors as regards the adsorption and reactivity of the intermediate radicals responsible for the formation of $CHCl_3$ and CH_4. The hydrogenolytic reactions of polyhalohydrocarbons are evidently consecutive in character.[19, 30, 41, 136]

3. Radical hydrogenation reactions. The hydrogenation of the surface radicals leads naturally to the formation of hydrogenolysis products. This has been demonstrated kinetically in studies[93, 102] where an increase in the proportion of the hydrogenolysis products with increase in the hydrogen concentration was established. The participation of the surface radicals in the hydrogenolytic reaction was confirmed directly by the study of the deuteriation of chloroalkanes.[102–104] On the one hand, the isotopic composition of the alkane formed indicates the structure of the surface radical involved in the hydrogenation and, on the other, it shows that this radical is indeed hydrogenated by hydrogen (deuterium).

4. Reactions involving the elimination of hydrogen atoms. By combining reactions (1)–(3), it is possible to obtain a wide variety of products of the catalytic hydrogenolysis of halogen-containing organic compounds. The contribution of the hydrogen elimination reactions to these processes is in most cases unimportant in view of the high strength of the C–H bonds.[150] Nevertheless, there is direct evidence for the involvement of these reactions in certain hydrogenolytic processes. Thus, in a study of the hydrogenolysis of chloroethane,[103] the problem arose which of the two intermediates, $[CH_3CH_2]_{ads}$ or $[CH_3CH]_{ads}$, actually participates in the process. It was found that, when the hydrogenation is carried out with deuterium and not hydrogen, the compound CH_3CHD_2 is formed as the product. This made it possible to make a choice in favour of the intermediate $[CH_3CH]_{ads}$. Furthermore, this result confirms the elimination of the hydrogen atom from the intermediate adsorbed species. This possibility has been discussed in connection with a study of the hydrogenolysis of fluorohydrocarbons on a palladium catalyst deposited on activated carbon.[30] The probability of the dissociation of the C–H bonds in these compounds are significantly higher than in other halo-derivatives because the C–F bond is characterised by the highest energies.

5. Polymerisation reactions. The occurrence of these reactions has been confirmed by the formation of polymeric products in certain catalytic hydrogenolytic processes. Thus, the formation of a wide range of products from C_1 to C_4 has been noted in a study of the hydrogenolysis of the compounds CH_nCl_{4-n} on Ni, Co, and Fe catalysts.[21] Polymeric products containing more than two carbon atoms are formed in the hydrogenolysis of chloromethane and dichloromethane on titanium films.[102] The mechanism of the formation of low-molecular-mass polymers has been little studied. One may postulate that this reaction proceeds via the interaction of surface carbene radicals with monoradicals. The acceleration of the formation of C_1–C_4 hydrocarbons from CO and H_2 on Ni, Co, and Fe catalysts following the addition of the compounds CH_nCl_{4-n} to the reaction mixture shows that the mechanism of the formation of the low molecular-mass polymers under the conditions of catalytic hydrogenolysis is similar to the mechanism of the Fischer–Tropsch synthesis.[21]

The data on the reactivities of halohydrocarbons in catalytic hydrogenolytic reactions are fragmentary. Nevertheless, the results of quantitative investigations permit the conclusion that the reactivities of different compounds in these reactions and hence the selectivities of the latter are determined by thermodynamic, polar, steric, and adsorption factors and also by the specificity of the catalytic system.

The antiparallel changes in the rate of hydrogenolysis of different bonds and in the energies of these bonds observed in a number of instances indicate that the thermodynamic factor exerts a decisive influence on the reactivities of the compounds and the selectivities of the reactions. Thus the decrease in the reactivities of chloroalkanes on a palladium catalyst in the sequence

$$\textit{tert}\text{-}C_4H_9Cl \gg \text{iso-}C_3H_7Cl > \text{n-}C_3H_7Cl > C_2H_5Cl,$$

is accompanied by an increase in the C–Cl bond dissociation energies in the same sequence.[104] It has also been shown that the C–Cl bond is more reactive in hydrogenolysis on the Pd/C catalyst than the C–F bond and that at the same time $D(C-Cl) < D(C-F)$.[152] We may note that the examples quoted are characteristic of platinum group metals, which do not exhibit a high specificity in relation to the adsorption of compounds of different nature.

The operation of the steric factor may be due either to the shielding of the reaction centre by bulky substituents of the substrates or by the dependence of the degree of accessibility of

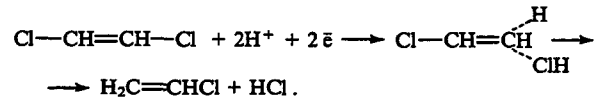
the catalyst active centres on the size of the species being adsorbed. Thus the inhibiting effect of *ortho*-substituents on the rate of hydrogenolysis of the C–Cl bonds of chlorobenzenes and chlorophenols is regarded as a result of the blocking effect of these substituents.[153, 154] The dependence of the accessibility of the catalyst active centre on the size of the reactant molecules is confirmed by the fact that the adsorption saturation of the catalyst surface by the organic reactant in the hydrogenolysis of *p*-chloronitrobenzene to *p*-chloroaniline is attained sooner than saturation by hydrogen.[65, 101]

The role of the polar factor is confirmed by the correlation between the rates of hydrogenolysis of the C–Cl bonds in *para*-substituted chlorobenzenes and polychlorobenzenes in the liquid phase on Pd/C and the electron-donating properties of the substituents in the aromatic ring.[155] This dependence has been attributed to the displacement of electron density towards the chlorine atom of the adsorbed substrate, which renders the attack on the latter by the electrophilic adsorbed hydrogen atom more effective. The antiparallel variation of the rate of hydrogenolysis of the C–Cl bonds and of the electron-donating capacities of the substituents in the vapour-phase process[156] indicates a fundamental difference between the mechanisms of the catalytic hydrogenolysis in the vapour and liquid phases. In particular, it has been suggested[156] that the key stage in the vapour-phase hydrogenolysis is nucleophilic attack by a surface hydride anion on the positively charged carbon atom of the C–Cl bond. In all the different mechanisms of the vapour-phase and liquid-phase processes, the polar character of the key stage is postulated in both cases and hence the dependence of the rate of hydrogenolysis on the presence or absence of polar substituents in the substrate.

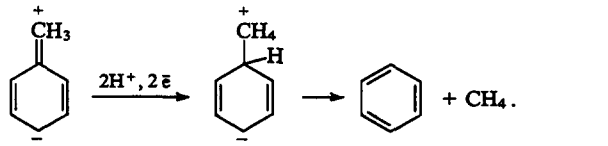
If the rate of catalytic hydrogenolysis is determined by Langmuir–Hinshelwood kinetics, then the composition of the products formed may be controlled by the adsorption capacities of the reactants or their functional groups. The data quoted above, indicating that methane is formed preferentially in the hydrogenolysis of tetrachloromethane, are evidence of the decisive influence of the adsorption factor on the composition of the products.

The inhibiting effect of hydrogen chloride on the hydrogenolytic processes observed in a number of studies has been usually attributed to the adsorption of this component on the surface and the blocking of the catalyst active centres. In order to prevent the blocking of the catalyst active centres by hydrogen chloride, certain processes are carried out in the presence of added alkalis, bases, or buffer mixtures [NaOH, KOH, NH_4OH, $NaOOCCH_3$–$N(C_2H_5)_3$, CH_3COONH_4–CH_3COOH, etc.].[41, 49, 51, 80, 155, 157] The hydrogenation of *o*-chloronitrobenzene is particularly instructive in this respect:[157] the hydrogenolysis of the C–Cl bond predominates in the presence of NaOH, whereas the reduction of the nitro-group predominates in its absence. These and other data suggest that there are active centres of different types on the catalytic surface, each of which is specific to a particular reaction.[44, 45]

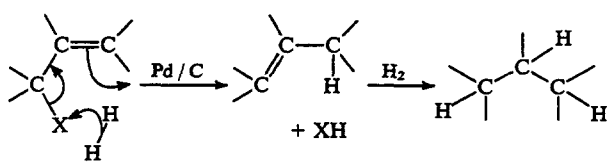
The specificity of the catalysts affects the relative contributions of the different reactions occurring under the conditions of the hydrogenolysis and especially the process selectivity. The role of the adsorption factor noted above is to some extent due to the specificity of the catalyst active centres in relation to the adsorption of the reactants. However, the nature of the specificity of catalytic systems is not restricted solely to adsorption interactions and in the general case one must take into account the structural characteristics of both the catalyst active centre and the reactant. This has been demonstrated in a study[136] where the hydrogenolysis of dichloroethenes on Pt/Al_2O_3 was investigated. The higher reactivity of the C–Cl bond in these reactants compared with chloroalkanes is due, according to the authors, to the stabilisation by the catalyst active centre of the quasi-tautomeric form of dichloroethene functioning as a surface intermediate in the hydrogenolytic reaction.



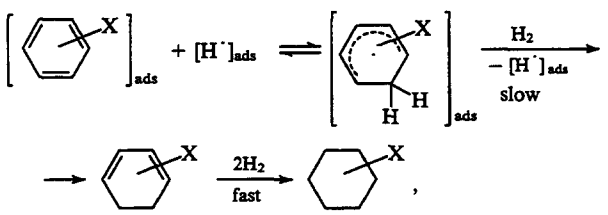
A similar approach has been used to account for the anomalously high reactivities of benzene derivatives.[136]



The increased mobility of the fluorine atom in the hydrogenolysis of allyl, vinyl, benzyl, and aryl fluorides has been attributed to the involvement of the double bond of the adsorbed compound in the substitution of fluorine by hydrogen.[158]

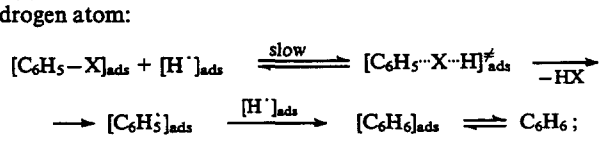


The above examples show that the specific features of the interactions on the surfaces of metallic catalysts are in many respects determined by the structural characteristics of the reactants. The soundest demonstration of this has been achieved in studies[44, 45] where competing reactions involving the hydrogenolysis of C–X bonds and the hydrogenation of the aromatic rings of the benzene derivatives C_6H_5X (X = OH, OC_2H_5, SC_6H_5, NH_2, NHC_6H_5, F, Cl, Br) were investigated on Ni–Mo, Co–Mo, and W–Mo catalysts deposited on aluminium oxide. The correlation between the rates of ring hydrogenation and the electron-donating properties of the substituents reflects to some extent the electrophilic character of this reaction, i.e.

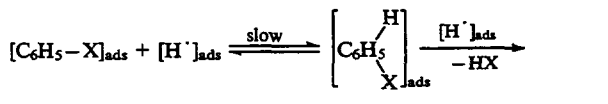


the successful outcome of which is determined by the stabilisation of the intermediate σ-complex. On the other hand, the high reactivity of the compounds C_6H_5X in hydrogenolysis is ensured by the presence of weak electron-donating substituents in the ring. One may postulate two possible pathways leading to hydrogenolysis on the catalytic surface:

(1) the abstraction of the substituent X by an adsorbed hydrogen atom:



(2) the substitution of the group X by a hydrogen atom via *ipso*-attack



Our attempts to observe a correlation between the rates of these reactions, on the one hand, and the heat of the hydrogenolytic reactions and the polarisability of the groups X, on the other, were unsuccessful. This confirms the need to take into

account the energetics of the interactions of the catalyst active centres with the components participating in the rate-limiting stages of the reactions.

Catalytic hydrogenolytic reactions are known to be structure-sensitive, which is manifested by the dependence of the specific activity of the catalyst on the accessibility and structures of the active centres.[144] The structural insensitivity of the hydrogenation reaction presupposes the independence of the activity of the catalytic centres of their structure. On the other hand, in hydrogenolysis the effective interaction between the catalyst active centre and the substrate requires the optimum combination of their structural properties and this is most clearly manifested in the presence of weak electron-donating substituents. The structural sensitivity of the hydrogenolytic reactions is confirmed by the numerous examples of the dependence of the specific activities of the catalysts on their dispersity.[99, 101, 129, 145, 146] The important role of the modification and of the methods of preparation of the hydrogenolysis catalyst which follows from this has been confirmed by the dependence of their activities and selectivities on the temperatures of their treatment by an inert gas and reductants,[19, 25, 39, 43, 85] the type of reductant,[19, 25, 39, 85, 103, 132] the presence of promoting additives,[19, 21, 24, 28, 29, 31, 132] and also on the treatment of the catalyst by gaseous reagents such HCl, Cl_2, air, H_2O, F_2, H_2S, etc.[19, 48, 60, 103, 125, 126, 128, 159] The importance of this method of preparation of the catalyst for the specific regulation of its activity has been demonstrated by the results of a study[47] where the possibility of the 'chemical grafting' of palladium ions on the Al_2O_3 surface with variation of the ionic character of the metal was demonstrated. A vigorous correlation between the ionic character of palladium and its activity was discovered.

The data on catalytic hydrogenolysis considered above indicate the need to formulate systematic studies in which kinetic experiments would be combined with the study of the properties of the catalytic surface, the adsorption equilibria, and the influence of impurities and modification on the activities and selectivities of the catalysts. A special study of the elementary steps on the surface is also required. From the practical point of view, it is important to direct the efforts of investigators to the study of the quantitative aspects of the deactivation and regeneration of the catalysts and to the development of catalytic systems resistant to the action of contact poisons.

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