Translated from *Uspekhi Khimii*, 52 455-482 (1983) U.D.C. 541.124.546.131.547.31

Hydrochlorination of Unsaturated Compounds

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The mechanism of the hydrochlorination of unsaturated compounds in condensed media is considered on the basis of modern data concerning the kinetics and products of the reaction and also the intermolecular interactions in the reaction system. It is shown that, like other addition processes, hydrochlorination can be carried out in non-polar media at low temperatures without the intermediate formation of ionic species, i.e. via a molecular mechanism. The factors which determine the competition between the ionic and molecular process mechanisms are analysed in detail.
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I. INTRODUCTION

The study of the addition of hydrogen halides to multiple bonds promoted the formulation of the fundamental concepts of modern chemistry. On the basis of the investigation of these reactions, ideas were developed concerning the involvement of carbonium ions and π-complexes in chemical reactions and have been used to formulate the familiar Markovnikov rule.

Hydrochlorination processes are of great theoretical and practical importance. The catalytic addition of hydrogen chloride to unsaturated compounds constitutes the basis of the large-scale syntheses of organochlorine products: ethyl chloride, vinyl chloride, methylchloroform, etc. Despite the large number of studies in this field, the process mechanism has been investigated inadequately. This is partly associated with the difficulty of obtaining reproducible kinetic data due to the catalytic influence of microimpurities on the rate and mechanism of the reaction.

The addition of hydrogen chloride to multiple bonds is usually considered mainly from the standpoint of an ionic mechanism[1,2]. Ideas concerning the ionic mechanism of the addition of halogen and hydrogen halides were formulated in the 1920's and have been developing vigorously up to the present time. On the other hand, many experimental facts do not fit within the framework of the traditional ideas. The possibility of hydrohalogenation without the preliminary ionisation of the reactants, i.e. via a molecular mechanism, has been noted by Shilov[3]. The high rate of addition at low temperatures in non-polar solvents and in the solid phase is consistent with the molecular mechanism[4]. Evidence in favour of the molecular mechanism of hydrohalogenation has been obtained in recent years in a number of investigations[5-7].

Thus the traditional ideas about the ionic mechanism of the addition of hydrogen chloride to olefins are of limited applicability. There is no doubt that the ideas formulated concerning the mechanism of electrophilic addition reactions, including hydrochlorination, will require re-examination and revision.

The mechanism of the hydrochlorination of olefins in the condensed phase is considered in the present review on the basis of modern data for the kinetics and products of reaction and also the intermolecular interactions in the hydrogen chloride–unsaturated compound–catalyst–solvent systems.

The factors determining the competition between the ionic and molecular hydrochlorination mechanisms are analysed in detail. As regards the gas-phase process, only data necessary for the discussion of the general aspects of hydrochlorination are examined. Among unsaturated compounds, attention has been concentrated on olefins.

II. PRODUCTS OF THE HYDROCHLORINATION OF UNSATURATED COMPOUNDS

1. Addition to Asymmetric Compounds

In the liquid phase the majority of unsaturated compounds slowly combine with hydrogen chloride. In the presence of catalysts, hydrochlorination takes place at a high rate at room and lower temperatures[8-10]. The most reactive olefins—3,3-dimethylbut-2-ene, 2-methylbut-2-ene,[11] and isobutene[12]—readily react with hydrogen chloride in the solid phase at low temperatures. The mode of addition to asymmetric compounds is determined by the Markovnikov rule in the absence of radical initiators: "the halogen adds to the least hydrogenated carbon atom, i.e. the atom subject to the greatest extent to the influence of other carbon moieties".[13] This rule holds in the gas[14] and solid[12] phases. Some examples of the validity of the Markovnikov rule in the liquid phase are presented below[15-22]:

$$CH_3CH=CH_2 \xrightarrow{HCl} CH_3CHClCH_3 ;$$
$$(CH_3)_2C=CH_2 \rightarrow (CH_3)_3CCl ;$$
$$CH_3CX=CH_2 \rightarrow CH_3CXClCH_3 ;$$
$$CH_2=CHCl \rightarrow CH_3CHCl_2 ;$$
$$(CH_3)_2C=CHCH_3 \rightarrow (CH_3)_2CClC_2H_5 ;$$
$$CH_3C(C_2H_5)=CH_2 \rightarrow (CH_3)_2CClC_2H_5 ;$$
$$C_6H_5CH=C(CH_3)_2 \rightarrow C_6H_5CH_2CCl(CH_3)_2 ;$$
$$CH_3C\equiv CH \rightarrow CH_3CCl=CH_2 \rightarrow CH_3CCl_2CH_3 ;$$
$$CH_3CH=CHCH=CH_2 \xrightarrow{DCl} \begin{cases} \rightarrow CH_3CH=CHCHClCH_2D ; \\ \rightarrow CH_3CHClCH=CHCH_2D . \end{cases}$$

If there are two different alkyl substituents at the double bond, then both possible addition products are formed in approximately equal amounts[23]. If one of the substituents is aromatic, then chlorine adds to the carbon atom linked to the aromatic ring. Thus, $C_6H_5CHClCH_2CH_3$ is obtained from $C_6H_2CH=CHCH_3$ [24] and $C_6H_5CCl=CHCH_3$ is obtained from $C_6H_5C\equiv CCH_3$.[25]

The addition of hydrogen halides to compounds containing simultaneously a double and a triple bond has been examined[26]. As a rule, the triple bond reacts more readily than the double bond. In the presence of a deficiency of hydrogen halide, vinylacetylene and allylacetylene give rise exclusively to products of addition to the triple bond.

Addition contrary to the Markovnikov rule (anomalous addition) is not characteristic of hydrogen chloride. The photochemical hydrochlorination of dodec-1-ene yields 10–30% of the anomalous addition product and 70–90% of the normal product[27]. 1-Chloropropane is formed as a side product in the high-temperature hydrochlorination of propene[28]. Small amounts of anomalous products have been obtained in the presence of peroxides[16]. The efficiency of the action of peroxides depends on the choice of solvent, the reactant ratio, and the nature of the unsaturated compound[29]. The yield of the anomalous addition products increases after the introduction of electron-accepting substituents into the molecule. Thus the contribution of the anomalous process is 12% for propene and as much as 29% for 3-chloropropene[30]. Addition contrary to the Markovnikov rule is associated with the involvement of radicals in the reaction. In contrast to the analogous reactions of hydrogen bromide, a quantitative yield is not observed in hydrochlorination.

Anomalous addition to acetylenic hydrocarbons under the influence of catalysts is attributed to the participation of organometallic compounds[31,32].

The Markovnikov rule formally breaks down in the hydrochlorination of 3,3,3-trifluoropropene in the presence of aluminium halides[33,34]. The formation of $CF_3CH_2CH_2Cl$ is associated with the high electronegativity of the CF_3 group and agrees with the modern interpretation of the Markovnikov rule[35].

The interaction of equimolar amounts of hydrogen chloride with diene compounds leads to the formation of 1,2- and 1,4-addition products. Under mild conditions (at low temperatures), 1,2-addition predominates in the absence of catalysts. Thus at 193 K but-1,3-diene reacts with HCl to form about 80% of the 1,2-addition product[36]. The hydrochlorination of isoprene in nitromethane at 198 K leads to the exclusive formation of 3-chloro-3-methylbut-1-ene.[19] 3-Chloro-1-phenylbut-1-ene has been obtained from 1-phenylbutadiene[37]. The formation of 1,4-addition products is promoted by an increase of temperature, an increase of the polarity of the medium, and the addition of water[22,38]. The reactions of dienes with hydrochloric acid in aqueous solutions lead to 1,4-addition[39–42]. In the hydrochlorination of dienes, the 1,2-addition products are probably formed initially and subsequently isomerise to the thermodynamically more stable 1,4-addition products[43,44].

The hydrochlorination of allene and many of its derivatives takes place in accordance with the Markovnikov rule[45,46]:

$$CH_2{=}C{=}CH_2 \xrightarrow{HCl} CH_2{=}CClCH_3 \xrightarrow{HCl} (CH_3)_2CCl_2 .$$

An exception is phenylallene[47] and allene homologues having two substituents at the double bond[46], a characteristic feature of which is protonation at the central carbon atom. A characteristic feature of allene is the formation of cyclic compounds together with the usual addition products[48,49]. Cyclodimerisation in the interaction with hydrogen chloride is characteristic also of certain acetylene derivatives[50–52].

Hydrochlorination may be accompanied by a rearrangement of the carbon chain of the organic compound in the intermediate stages of the process where the structure of the addition products does not correspond to the structure of the initial unsaturated compound. For example, the hydrochlorination of *cis*- and *trans*-1-phenylbuta-1,3-dienes yields a single product—*trans*-1-methyl-3-phenylallyl chloride[53].

The gas-phase hydrochlorination of but-1-ene in the presence of the $CaCl_2$ catalyst leads to the formation of t-butyl chloride. But-2-ene gives rise to the non-rearranged product—2-chlorobutane—under the same conditions[54].

The rearrangement of an unbranched olefin is a rare phenomenon. On the other hand, the products of the hydrochlorination of branched olefins containing a tertiary carbon atom in the α-position relative to the double bond frequently do not correspond to the structure of the initial compound. For example, two products of the reaction via the mechanism[55]

$$H_3C\diagdown\!\!\diagup CHCH{=}CH_2 \xrightarrow{HCl} \begin{cases} \rightarrow (CH_3)_2CHCHClCH_3 & (33–40\%) \\ \rightarrow CH_3CH_2C(CH_3)ClCH_3 & (67–60\%) \end{cases},$$

were obtained in the hydrochlorination of 3-methylbut-1-ene. A rearrangement of the carbon chain occurs in the hydrochlorination of 3,3-dimethylbut-1-ene[29,56]. The ratio of the normal and rearranged chlorides is approximately 1:1 in a non-polar medium and changes to 1:6 on passing to the polar nitromethane[55]. The hydrochlorination of chlorine-containing olefins is also accompanied by rearrangements[57]:

$$CH_2{=}CClC(CH_3)_3 \xrightarrow{HCl} \begin{cases} \rightarrow CH_3CCl_2C(CH_3)_3 , \\ \rightarrow (CH_3)_2CClCCl(CH_3)_2 , \\ \rightarrow ClCH_2CH(CH_3)CCl(CH_3)_2 . \end{cases}$$

The mechanism of the rearrangement of the carbon chain is examined below (Section V). The literature data[55–57] show that the rearrangement takes place at intermediate stages of the reaction and is not associated with the isomerisation of the final product. Rearrangements of the carbon skeleton are also characteristic of the hydrochlorination of norbornene and related compounds[58–60].

Table 1. Stereochemistry of the hydrochlorination of arylacetylenes.

Hydrocarbon	Solvent	Catalyst	Yield, %		Refs.
			cis	*trans*	
$DC{\equiv}CC_6H_5$	CH_2Cl_2	$ZnCl_2$	70	30	[65]
$DC{\equiv}CC_6H_5$	CH_3COOH	—	60	40	[65]
$DC{\equiv}CC_6H_5$	CH_3NO_2	$ZnCl_2$	55	45	[65]
$DC{\equiv}CC_6H_5$	sulpholane	$ZnCl_2$	50	50	[65]
$DC{\equiv}CC_6H_5$	sulpholane	—	75	25	[65]
$CH_3C{\equiv}CC_6H_5$	CH_3COOH	—	67–78	11–19	[66]
$CH_3C{\equiv}CC_6H_5$	CH_2Cl_2	$ZnCl_2$	70	30	[25]
$C_2H_5C{\equiv}CC_6H_5$	CH_2Cl_2	$ZnCl_2$	80	20	[25]
$(CH_3)_2CHC{\equiv}CC_6H_5$	CH_2Cl_2	$ZnCl_2$	95	5	[25]
$(CH_3)_3CC{\equiv}CC_6H_5$	CH_2Cl_2	$ZnCl_2$	100	0	[67]
$C_6H_5C{\equiv}CC_6H_5$	CH_2Cl_2	$ZnCl_2$	100	0	[68]

2. Stereochemistry of the Addition of Hydrogen Chloride

The stereochemistry of the hydrochlorination products is determined by the structure of the unsaturated compound and the reaction conditions. *trans*-Addition is characteristic of acetylene and its aliphatic derivatives[61–64]. Table 1 shows that there is no trans-stereospecificity in the hydrochlorination of tolane and other arylacetylenes. The yield of the *cis*-product increases steadily with increase of the bulk of the alkyl substituent. As the solvating capacity of the solvent becomes more pronounced, the ratio of the *cis*- and *trans*-additions in the catalytic hydrochlorination of tolane approaches 1.

Data on the stereochemistry of the products of the hydrochlorination of olefins are summarised in Table 2. The characteristic features of the process stereochemistry are difficult to trace clearly. A classification of olefins on the basis of the stereochemistry of their hydrohalogenation has been proposed in a review[69], where compounds with a double bond have been divided into four groups: (1) arenes and dienes yielding *cis*-addition products; (2) cyclic olefins and olefins without conjugated bonds, for which *trans*-addition is a characteristic process; (3) bicyclic olefins forming *cis*-products; (4) α,β-unsaturated carbonyl compounds, which combine with hydrogen halides exclusively in the *trans*-position. A deficiency of this classification consists in the fact that no account has been taken of the influence of conditions on the stereochemistry of the reaction which is extremely important, as can be seen from Table 2.

Table 2. Stereochemistry of the hydrochlorination of olefins.

Olefin	Solvent	ε	T, K	Yield, %			Refs.
				cis	*trans*	other products	
1-Methylcyclopentene	CH_3NO_2	38.6	298	4	96	0	[55]
1,2-Dimethylcyclopentene	C_5H_{12}	1.8	273	20	80	0	[70]
1,2-Dimethylcyclopentene	C_5H_{12}	1.8	195	5	95	0	[70]
Cyclohexene	CH_3COOH	6.2	298	3—4	14—28	—	[71]
Cyclohexene	CH_3COOH	6.2	353	18	18	64	[71]
1,2-Dimethylcylohexene	C_5H_{12}	1.8	298	14	86	0	[72]
1,2-Dimethylcyclohexene	C_5H_{12}	1.8	273	8	92	0	[72]
1,2-Dimethylcyclohexene	CH_3COOH	6.2	298	37—40	6—18	42—58	[72]
1,2-Dimethylcyclohexene	CH_3COCl	15	273	76	24	0	[72]
1,2-Dimethylcyclohexene	CH_2Cl_2	8.9	298	64—74	26—36	0	[72]
1,2-Dimethylcyclohexene	CH_2Cl_2	8.9	177	88	12	0	[72]
1,2-Dimethylcyclohexene	HCl (liq.)	9.1	177	87	13	0	[73]
1,2-Dimethylcyclohexene	$(C_2H_5)_2O$	4.2	273	5	95	0	[73]
1,2-Dimethylcyclohexene	sulpholane	44	298	53	47	0	[72]
1,2-Dimethylcyclohexene	CH_3OH	32.6	298	9—30	70—91	0	[72]
$\Delta^{9,10}$-Octalin	CH_2Cl_2	8.9	195	54	46	0	[74]
$\Delta^{9,10}$-Octalin	CH_2Cl_2	8.9	177	61	39	0	[73]
$\Delta^{9,10}$-Octalin	HCl (liq.)	9.1	177	64	36	0	[73]
$\Delta^{9,10}$-Octalin	$(C_2H_5)_2O$	4.2	273	2	98	0	[73]
$\Delta^{9,10}$-Octalin	aq.HCl	—	273	6	94	0	[74]
Indene	CH_2Cl_2, C_5H_{12}	—	195	50	50	0	[75]
Acenaphthene	CH_2Cl_2	8.9	273	85	15	0	[76]
Norbornene	various	—	195	49	1	50	[58]
Apobornylene	various	—	195	90	0	10	[60]
Bornylene	various	—	195	100	0	0	[59]

The data in Table 2 agree with the above classification[69] for norbornene and other bicyclic compounds, for which only *cis*-addition does indeed occur. For indene, acenaphthalene, norbornene, and related compounds in the absence of steric hindrance in weakly polar and non-polar media, the preferential formation of the *cis*-product has been observed. The exclusive formation of the *trans*-product has not been observed for cyclohexene and cyclopentene homologues[72]. The direction of the process varies as a function of the choice of the solvent. In the case of 1,2-dimethylcyclohexene an increase of the polarity and ionising capacity of the solvent promotes *cis*-addition. It has so far been impossible to formulate a general rule governing the influence of the medium on the stereochemistry of the hydrochlorination. Treatment of the results is hindered by the influence of steric factors on addition to systems containing the cyclopentene or cyclohexene ring.

Additional possibilities for the formation of stereoisomers arise in the reactions of dienes. Thus 1,4-addition to conjugated dienes can lead to *cis*- or *trans*-alk-2-enes. The hydrochlorination of 2,3-dichlorobuta-1,3-diene[77] and *trans*-penta-1,3-diene[22] results in the formation of mainly the *trans*-isomers. Both possible products have been noted in the hydrochlorination of chloroprene[78].

Hydrochlorination at room and elevated temperature, particularly in the presence of catalysts, is frequently complicated by the polymerisation[30,36,79–83] and isomerisation[45,46,72] of the olefins as well as the decomposition of the addition products[10,84] occurring under the influence of the same catalysts. The addition of hydrogen chloride in hydroxylated solvents competes with the addition of the solvent[56,57,71,85,86].

III. KINETICS OF HYDROCHLORINATION

1. Kinetics of the Gas-Phase Reaction

Non-catalytic hydrochlorination in the gas phase takes place slowly. The reaction of isobutene with hydrogen chloride at 300–500 K is described by a second-order kinetic equation, whose rate constant can be represented in the following form[87]:

$$k_2 = 10^8 \exp(-28800/RT)\ (\mathrm{dm^3\ mol^{-1}\ s^{-1}}).$$

At high temperatures the equilibrium is displaced towards the starting materials and the kinetic parameters of the majority of the hydrochlorination processes have been calculated from data for the molecular elimination of HCl from the corresponding alkyl chlorides. The results of such calculations are presented below[14]:

Olefin	C_2H_4	C_3H_6	iso-C_4H_8
E, kJ mol^{-1}	167	141	106
lg$A$ (dm^3 mol^{-1} s^{-1})	8.8	7.8	6.1

The reactivity of olefins increases rapidly with increase of the number of substituents at the double bond. The activation energy for addition contrary to the Markovnikov rule is higher by at least 30 kJ mol^{-1} than for normal addition[14].

Extrapolation of the elimination data to room and lower temperatures leads to the conclusion that the rate of the gas-phase hydrochlorination of the majority of olefins should be negligible under such conditions. However, recent studies have shown[88,89] that the hydrochlorination of many olefins proceeds at an appreciable rate at 300 K and below and that the kinetic process parameters are different from those found earlier[14,87]. The hydrochlorination of isobutene is accelerated on passing from 373 K to lower temperatures[88]. The rate of the process is higher by a factor of 10^9 than might have been expected on the basis of data for the high-temperature process. The gas-phase hydrochlorination of allene is described by a second-order equation and takes place with zero activation energy[45]. The following equation has been obtained for the low-temperature hydrochlorination of propene in the gas phase[89]:

$$v = k_4 [C_3H_6] [HCl]^3 .$$

A negative temperature coefficient was observed in the reaction: the rate of the reaction at 293 K is three times higher than at 373 K. Traces of water, nitrogen oxides, and the surface of the vessel have a catalytic influence on the reaction; quantitative data have not been obtained for the catalytic process.

The data for the reaction kinetics permit the conclusion that in the gas phase the hydrochlorination takes place via two pathways. At high temperatures a bimolecular reaction with a high activation energy takes place. At temperatures below 373 K another pathway predominates, for which the

effective activation energies are negative or close to zero and whose rate is described by a second-order or a higher-order equation.

2. Kinetics of the Non-catalytic Reaction in the Liquid Phase

The kinetic equation for the liquid-phase hydrochlorination depends on the solvent selected. In non-polar solvents the kinetics are complex. For example, the hydrochlorination of isobutene is approximately described by the equation[90]

$$v = k_4[C_4H_8][HCl]^3 \ .$$

The rate of the process at 273 K is higher than at 195 K. However, it has been noted that preliminary cooling of the reaction mixture to 195 or 77 K leads to an increase of the degree of reaction on subsequent heating to 273 K. A negative temperature coefficient has been observed in the hydrochlorination of 1-methyl-2-methylenenorbornene in pentane[91]. Overall, the hydrochlorination kinetics in polar media have been inadequately investigated.

An increase of the polarity of the solvent leads in a number of instances to an increase in the rate of hydrochlorination. For example, on passing from pentane to methylene chloride, the time required for the quantitative addition of HCl to norbornene is considerably reduced[92]. Dilution of acetic acid with cyclohexane retards the hydrochlorination of 1-phenylpropyne[66]. Instances are known where an increase of the dielectric constant of the solvent ε has a weak influence on the rate of hydrochlorination. Thus in pentane and methylene chloride a specific degree of hydrochlorination of acenaphthene is attained during the same period[76]. The rate of hydrochlorination of a number of dienes depends little on the dielectric constant[93]. The retardation of hydrochlorination is sometimes observed on passing to more polar media. The rate of hydrochlorination of hex-3-ene and cyclohexene diminishes in the following sequence of solvents: heptane > xylene > nitrobenzene > ether[94]. The authors[94] attribute this influence of the medium to the electron-donating capacity of the solvents and specific solvation and not to the dielectric constant of the solvent.

The kinetic equation for hydrochlorination in polar media can be represented in the following form:

$$v = k_2[RH][HCl] + k_3[RH][HCl]^2 \ . \qquad (1)$$

The ratio of the two terms of Eqn.(1) is determined by the nature of the solvent. In highly polar solvents without hydroxy-groups such as nitromethane, the hydrochlorination of various olefins is described by an equation of third order overall[19,55,95]. The third order is characteristic of the hydrochlorination of isoprene in the absence of a third component[96]. In acetic acid both terms of Eqn.(1) are significant. The third and higher orders have been observed in the hydrochlorination of 1-phenylpropyne[66] and hex-3-yne[56]. In the case of olefins in acetic acid a termolecular hydrochlorination process competes with the bimolecular reaction. The interpretation of the reaction kinetics in acetic acid is hindered by the inadequate accuracy of the kinetic data[85]. The most reliable results appear to be those of the studies of Okuyama and co-workers[47,53], where the kinetics of the hydrochlorination of dienes were investigated over a wide range of hydrogen chloride concentrations. A change in the kinetic equation for the reaction with increase of the HCl concentration was observed. For phenylallene, the reaction is described by an equation of second order overall at an HCl concentration of 0.1–0.25 M and of third order at 0.64–1.3 M. Hydrochlorination in acetic acid is accelerated in the presence of salts containing the Cl^- anion[56,85].

The hydrochlorination of propene in organochlorine solvents is described by a second-order equation, of first order with respect to each reactant[97]. In the analysis of the kinetic equations for hydrochlorination in organochlorine solvents, it is necessary to take into account the possibility of the self-association of hydrogen chloride[98].

Table 3. Kinetic parameters of liquid-phase hydrochlorination.

Hydrocarbon	Solvent	n*	$-\Delta H$, kJ × × mol^{-1}	$-\Delta S$, J × × mole^{-1} K^{-1}	Refs.
Propene	$C_2H_2Cl_4$	2	39	162	[97]
Propene	$C_2H_3Cl_3$	2	25	229	[97]
Propene	$C_2H_4Cl_2$	2	27	213	[97]
Propene	$C_3H_6Cl_2$	2	43	160	[97]
Hex-3-yne	CH_3COOH	3.5	96	84	[56]
Hex-3-yne	$(CH_3)_4NCl+CH_3COOH$	1	60	138	[56]
Phenylallene	CH_3COOH	3	81	53	[47]
1-Phenylbuta-1,2-diene	CH_3COOH	3	74	69	[53]
cis-1-Phenylbuta-1,3-diene	CH_3COOH	3	69	22	[53]
trans-1-Phenylbuta-1,3-diene	CH_3COOH	3	89	47	[53]

*Here n is the overall reaction order.

The overall order of certain liquid-phase hydrochlorination reactions and their activation parameters are listed in Table 3. The kinetic data make it possible to identify the main types of non-catalytic hydrochlorination in the liquid phase. The processes proceed at a low rate in non-polar solvents, are described by high-order equations, and can be accelerated at low temperatures. The kinetics of hydrochlorination in non-polar media resemble those of the low-temperature gas-phase reaction. In a polar solvent the hydrochlorination process proceeds via two pathways described by second- and third-order equations. The activation energies are in this instance 25–100 kJ mol^{-1}. The relative contributions of the processes depend on the nature of the solvent and the reactants.

The reactions of concentrated hydrochloric acid, in which the main bulk of hydrogen chloride is dissociated, must be considered separately. For example, the order of the reaction of cyclohexene and methylcyclohexenes with respect to HCl is first and that with respect to the olefin is first or zero. The observed activation energies are 32–76 kJ mol^{-1}.[99] Activation energies of 4 and 10 kJ mol^{-1} have been obtained for the 1,2- and 1,4-addition respectively in the hydrochlorination of isoprene in hydrochloric acid[42].

3. Kinetics of Catalytic Hydrochlorination

Hydrochlorination is catalysed by various substances. The simplest catalyst is water. Its catalytic action has been observed in the hydrochlorination of isoprene[38], isobutene[90], and dicyclopentadiene[100]. The acceleration of the addition and the increase of the yield of the *trans*-product in the presence of water have been noted for a series of reactions in acetic acid[72,85,101]. A slight acceleration of the hydrochlorination of 3,3-dimethylbut-1-ene has been observed after the addition of water to a concentration of 0.6 M, while a further increase of its concentration to 2.5 M retards the reaction[56]. No kinetic data are available for the influence of water on the rate of hydrochlorination.

Metal halides are the most effective hydrochlorination catalysts. In the presence of the halide MX_n, the kinetic equation for hydrochlorination usually assumes the form

$$v = k_3 [RH] [HCl] [MX_n] \quad . \qquad (2)$$

It describes satisfactorily the kinetics of the hydrochlorination of ethylene in nitrobenzene[102], of vinyl chloride and the isomeric 1,2-dichloroethylenes in the presence of $AlCl_3$,[103] of propene in the presence of $FeCl_3$,[104] and of styrene in the presence of $SnCl_4$.[105] A decrease of the reaction order with respect to the olefin in the presence of an excess of the latter has sometimes been observed[104]. A decrease of the reaction order with respect to the catalyst with increase of the $SnCl_4$ concentration above 0.04 M has been noted in the hydrochlorination of styrene[105].

Overall orders in excess of the third are rarely encountered for the catalytic process. An overall fourth order, second with respect to the olefin, has been noted for the catalytic hydrochlorination of vinyl chloride under the influence of $FeCl_3$.[106] An increase of the order with respect to the catalyst occurs in the hydrochlorination of ethylene in the presence of $AlCl_3$ in organochlorine solvents[104] and of acetylene in the presence of CuCl in aqueous solution[107].

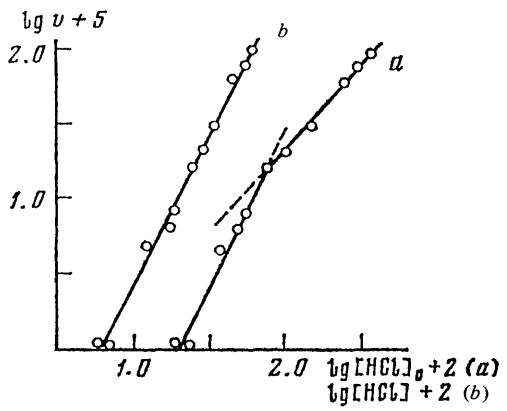


Figure 1. Dependence of the logarithm of the initial rate of hydrochlorination of cyclohexene in the presence of $SnCl_4$ in hexane at 183 K on the logarithm of the initial concentration of hydrogen chloride $[HCl]_0$ (*a*) or on the logarithm of the concentration of "free" hydrogen chloride [HCl] (*b*).[108,109]

The catalytic hydrochlorination of cyclohexene in non-polar and weakly polar media has been investigated taking into account complex formation in the system[6,108,109]. It is seen from Fig. 1*a* that the kinetics of the reaction with a variable order with respect to hydrogen chloride are described satisfactorily by the equation for a fourth-order reaction:

$$v = k_4 [C_6H_{10}] [HCl]^3 [SnCl_4] \quad , \qquad (3)$$

where [HCl] is the concentration of hydrogen chloride not bound in associated species, which can be calculated from the material balance equation

$$[HCl]_0 = [HCl] + 2K_{(HCl)_2} [HCl]^2 + K_{C_6H_{10}\cdot HCl} [C_6H_{10}] [HCl] + K_{SnCl_4\cdot HCl} [SnCl_4] [HCl] .$$

The $\lg v - \lg [HCl]$ relation (Fig. 1*b*) does not have a break and the slope of the straight line is 2. At low temperatures and high HCl concentrations, where $[HCl]^2 = [HCl]_0/2K_{(HCl)_2}$, Eqn. (3) becomes identical with the kinetic equation for a third-order reaction:

$$v = k_4/2K_{(HCl)_2} [C_6H_{10}] [HCl]_0 [SnCl_4] = k_3 [C_6H_{10}] [HCl]_0 [SnCl_4] .$$

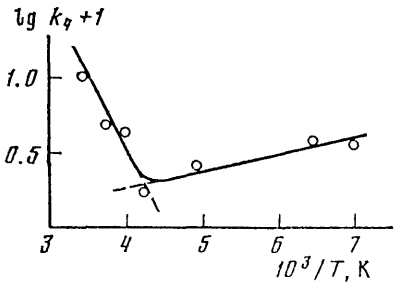


Figure 2. Dependence of the logarithm of the rate constant k_4 for the hydrochlorination of cyclohexene in the presence of $SnCl_4$ in hexane on the reciprocal of temperature[109].

Table 4. Activation energies for the liquid-phase catalytic hydrochlorination.

Hydrocarbon	Solvent	Catalyst	*E*, kJ mol^{-1}	Refs.
Ethylene	$C_6H_5NO_2$	$AlCl_3$	70	[102]
Acetylene	H_2O, NH_4Cl	CuCl	42	[107]
Propene	$C_2H_2Cl_4$	$FeCl_3$	40	[104]
Vinyl chloride	$C_2H_2Cl_4$	$AlCl_3$	56	[106]
Vinyl chloride	$C_2H_2Cl_4$	$FeCl_3$	88	[106]
cis-Dichloroethylene	$C_2H_2Cl_4$	$AlCl_3$	73	[106]
trans-Dichloroethylene	$C_2H_2Cl_4$	$AlCl_3$	84	[106]
Styrene	CCl_4	$SnCl_4$	39	[105]
Cyclohexene	C_6H_{14}	$SnCl_4$	18 *	[109]
Cyclohexene	C_6H_{14}	$SnCl_4$	0 **	[109]
Cyclohexene	CCl_4	$SnCl_4$	0	[109]
Cyclohexene	CH_2Cl_2	$SnCl_4$	14	[109]
Cyclohexene	CH_2Cl_2—CCl_4	$SnCl_4$	10	[109]

*In the temperature range 233–293 K.
**In the temperature range 143–203 K.

On passing from hexane to methylene chloride, the reaction rate increases slightly and at 183 K is almost independent of the dielectric constant of the medium.

The temperature variation of the reaction rate constant k_4 is illustrated in Fig. 2 in terms of the variables of the Arrhenius equation, the Figure showing that the activation energy for the reaction decreases with decrease of temperature.

A complex form of the temperature variation of the rate of the process has also been observed in the catalytic hydrochlorination of ethylene in ethyl chloride: at 273 and 163 K the reaction is slow, the rate of the process being a maximum at 213–218 K.[81]

In the majority of cases, the rate constants for catalytic hydrochlorination obey the Arrhenius equation. The activation energies for a number of homogeneous catalytic hydrochlorination reactions are listed in Table 4. Evidently, for

the simplest unsaturated compounds, the activation energies are 40–90 kJ mol^{-1}. For the more reactive olefins (cyclohexene and styrene), the activation energies are less than 40 kJ mol^{-1}. For cyclohexene in non-polar solvents at low temperatures, the activation energy for hydrochlorination is close to zero. In a more polar solvent (methylene chloride) the activation energy increases.

4. The Isotope Effect

The isotope effect in hydrochlorination in polar and hydroxylated media varies in the range 0.7–2.3. For example, isotope effects of 1.3 for cyclohexene[71], 1.15 for 3,3-dimethylbut-1-ene[56], 1.4 for styrene[56], and 1.54 and 2.3 for *cis*- and *trans*-1-phenylbuta-1,3-dienes respectively[53] have been obtained in acetic acid. In nitromethane, HCl adds to 1-methylcyclopentene 1.6 times more slowly than DCl.[55]

When the polarity of the medium is reduced, the ratio k_H/k_D increases. For catalytic hydrochlorination of cyclohexene (at 183 K), the isotope effect changes from 0.7 to 4.2 on passing from methylene chloride to hexane[110].

The kinetic characteristics of the hydrochlorination reactions of unsaturated compounds—a high, frequently variable, reaction order, a negative temperature coefficient, and an activation energy close to zero—may be due to the association of the reactants in the reaction system.

IV. INTERMOLECULAR INTERACTIONS IN HYDROGEN CHLORIDE–UNSATURATED COMPOUND–CATALYST–SOLVENT SYSTEMS

In systems containing hydrogen chloride, an unsaturated compound, and a catalyst in a condensed phase, a number of complex formation processes take place. The ability of hydrogen chloride to form hydrogen bonds, which leads to self-association, plays an important role.

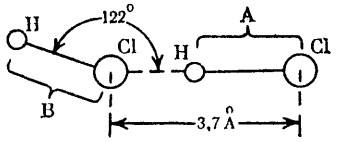
1. Self-Association of Hydrogen Chloride

The polymeric species $(HCl)_n$ are formed in all the phase states. In the gas phase, $n = 2$. The study of gaseous HCl by infrared spectroscopy showed that at 293 K and 10 atm approximately 1% of the substance exists in the form of the dimer $(HCl)_2$. The enthalpy of dimerisation is close to −10 kJ mol^{-1}.[111]

In polar and hydroxylated solvents, the complex formation reaction with the solvent suppresses the self-association of hydrogen chloride. In a non-polar inert solvent (1,2-dibromotetrafluoroethane) at an HCl concentration below 0.5 M, the dominant type of self-association is the dimerisation of HCl. The dimerisation equilibrium constant is 0.84 litre mol^{-1} at 293 K and the enthalpy and entropy of the process are −8 kJ mol^{-1} and −31 J mol^{-1} K^{-1}. The degree of self-association increases with decrease of temperature: 70% of the hydrogen chloride molecules are dimerised at 173 K for [HCl] = 0.5 M.[98]† In organochlorine solvents complex formation with the solvent competes with the dimerisation of hydrogen chloride and the degree of dimerisation of HCl decreases[98,112].

The self-association of hydrogen chloride in the solid phase has been observed in an infrared spectroscopic study of HCl in an argon matrix at 10–30 K; the spectra show bands due to the hydrogen chloride dimers, trimers, and tetramers[113–115]. In order to obtain isolated hydrogen halide molecules, a 400-fold excess of a diluent is necessary[116].

Two types of associated hydrogen chloride species—linear and cyclic—have been considered in the literature. In the trimers and tetramers all the HCl molecules are equivalent, which indicates a cyclic structure. In the dimer the HCl molecules have different force constants[115]. The study of the structure of the hydrogen chloride dimer by pulsed ^1H NMR showed that it is as follows[117]:



The distance between the hydrogen atoms is 3.3 Å. The greater stability of the linear structure compared with the cyclic structure is consistent with the results of a quantum-mechanical calculation[118]. In the dimer there is charge transfer from molecule B to molecule A. The negative charge is concentrated on the chlorine atom of the A molecule and the positive charge is distributed between the remaining atoms.

2. Complexes of Hydrogen Chloride with Unsaturated Compounds

The formation of molecular 1:1 complexes in solid mixtures of hydrogen chloride with olefins and acetylenes has been demonstrated in studies of fusion diagrams[11,119]. Complexes of the type 2HCl.RH are also known for a number of unsaturated compounds and the complexes 4HCl.RH are known for alkylacetylenes[119]. Application of low-temperature infrared spectroscopy led to the discovery of the complexes HCl.2RH.[120] The enthalpy of formation of the 1:1 complexes in the solid phase is between −10 and −22 kJ mol^{-1} according to infrared spectroscopy[121]. The contribution of pair or collective interactions to the stabilisation of such complexes is low[122,123]. The 1:1 complexes are the most stable in the solid phase[120,123].

In the liquid and gas phases these complexes have been inadequately studied. The first quantitative data were obtained as late as 1978 using low-temperature infrared spectroscopy[124,125]. In liquid nitrogen at 93 K the equilibrium constant for the complex formation with hydrogen chloride increases from 8 to 6×10^3 litre mol^{-1} on passing from ethylene to 2,3-dimethylbut-2-ene, while the enthalpy of complex formation changes from −5.8 to −13.4 kJ mol^{-1}.

The degree of charge transfer in the complexes of hydrogen chloride with olefins is considerable and amounts to 0.1 to 0.3 of a unit electronic charge[121]. There are no direct experimental data for the disposition of the molecules in these complexes. It has been suggested that the hydrogen chloride molecule is arranged at right angles to the plane of the olefin. On the basis of the satisfactory correlations between the shift of the vibration frequencies and the enthalpy of complex formation characteristic of hydrogen-bonded complexes, it is believed that the interaction in such complexes involves a hydrogen bond[122,126,127]. However, quantum-mechanical calculation by the CNDO/3 method showed

†During the preparation of this review for the press, B.Desbat and P.V.Huong published their study (Bull.Soc. chim.France, 1981, 301), in which the dimerisation of hydrogen chloride in the liquid phase was additionally confirmed by infrared and Raman spectroscopy and the structure of the dimers was considered.

that the configuration in which the hydrogen chloride molecule assumes the disposition with the chlorine atom pointing towards the olefin is the most stable[128]. The negative charge is concentrated on the chlorine atom and the positive charge is distributed over the molecule of the unsaturated compound. The calculated degree of charge transfer in the ethylene–HCl complex is close to 0.1.

Several types of orientation can probably occur in complexes of hydrogen chloride with olefins. Comparison of the experimental entropy for the formation of the ethylene–hydrogen chloride complex with the values calculated for different models of the complexes showed that agreement can be achieved only on the assumption that internal movements occur in the complex, namely rotation or vibration, with a high amplitude[129]. There is apparently no rigorously fixed molecular orientation in the complexes of hydrogen chloride with olefins and their structures are extremely labile.

3. Complexes with Participation of the Solvent

The majority of organic solvents form complexes with hydrogen chloride. We shall confine ourselves to a brief consideration of the most important types of interactions.

The formation of complexes of HCl with compounds of the benzene series was observed in a study of fusion diagrams[119] and of the solubility of gaseous hydrogen chloride in aromatic compounds[130]. The thermodynamic characteristics of the complex formation reactions are comparable to those obtained for olefins. For example, the equilibrium constant for the formation of the benzene–HCl complex at 293 K is 0.17 litre mol^{-1} and $-\Delta H = 12.5$ kJ mol^{-1}.[131] The nature of the bonding in the complexes is various. In the case of olefins charge transfer plays the main role, while for aromatic compounds dipole–quadrupole and dispersion interactions are important[126]. The higher energy of the interaction of HCl with benzene in the presence of water indicates the possibility of the formation of ternary complexes[132].

Organochlorine compounds form hydrogen-bonded complexes with hydrogen chloride[98,112,133,134]. The enthalpies of formation of such complexes are in the range between −6 and −10 kJ mol^{-1} and the equilibrium complex formation constants at room temperature are approximately 0.1 litre mol^{-1}.

Substances containing ether or carbonyl oxygen form more stable complexes with hydrogen chloride. When ethers interact with hydrogen chloride, 1 : 2 complexes[136] as well as associated species with three, four, and six HCl molecules[137] are formed in addition to the well known 1 : 1 complexes[135]. In the interaction with aromatic ethers, the coordination involves the oxygen atom[138]. The enthalpies of formation of 1 : 1 complexes of HCl with ethers are in the range between −23 and −30 kJ mol^{-1}.[131] The 1 : 2 complexes are weaker and are characterised by $-\Delta H \cong 10$–16 kJ mol^{-1}.[136] Experimental and computational studies on the structures of such complexes have been described[138,139,140]. When HCl interacts with ethers, there is a possibility of the protonation of the latter with the formation of onium salts[140,141]. However, HCl_2^- ions could not be detected by NQR in the solid phase, which is inconsistent with the hypothesis of spontaneous protonation[138].

The complexes of hydrogen chloride with other oxygen-containing compounds, including water, have been considered in a number of studies[142–146].

The universal ability of hydrogen chlorides to form complexes is indicated by the observation of intermolecular interaction of HCl with argon[147] and nitrogen[148].

The interaction between unsaturated compounds and an organochlorine solvent (CCl_4) is indicated by the increase of the negative enthalpy of mixing compared with hydrocarbons without a double bond[149]. For aromatic hydrocarbons and olefins, the enthalpies of formation of their complexes with CCl_4 are −(1–5) kJ mol^{-1}.[150]

4. Complexes of Metal Halides in Hydrochlorination

The typical hydrochlorination catalysts, namely metal halides, are strong complex-forming agents. The stability of the complexes of Group IV metal halides is low. Thus the enthalpy of formation of the complex of hydrogen chloride with tin tetrachloride in a non-polar medium is −6 kJ mol^{-1}.[112] The shifts of the stretching vibration band of HCl in $TiCl_4$ and CCl_4 relative to the gas phase are approximately the same, which indicates the similarity of the bond energies[151]. Such complexes can be formed as a result of the usual classical van der Waals interactions. The enthalpies of reaction of HCl with a number of metal halides, estimated from adsorption measurements, are −8 kJ mol^{-1} for solid $BiCl_3$, −9 kJ mol^{-1} for $ZnCl_2$, and −15 kJ mol^{-1} for $CdCl_2$.[152] The Group III metal salts form more stable complexes with HCl: the enthalpies of formation of such complexes are −16 and −41 kJ mol^{-1} for $FeCl_3$ and $AlCl_3$ respectively[104]. The most probable composition of the complex of HCl with $AlCl_3$ corresponds to the formula $HAl_2 \cdot Cl_7$;[153] the structure of the complex depends on the nature of the solvent[104,154].

The majority of metal halides form complexes also with unsaturated compounds and their strength varies within wide limits. A high stability is characteristic of aluminium halide complexes. The appreciable shift of the stretching vibration bands of the double bonds in the ethylene, propene, cyclohexene, and other olefin complexes with $AlHal_3$ indicates perturbation of the π-electron cloud[155,156]. The structure of a typical π-complex with coordination of the aluminium atom to the centre of the double bond has been proposed for such complexes. Aluminium halides are involved in complexes of this kind in a monomeric form, which indicates their stability. The equilibrium constant for the formation of the propene–$AlCl_3$ complex is 7.3 litre mol^{-1} at 293 K and the enthalpy of formation is approximately −100 kJ mol^{-1}.[104]

The complexes of Group IV metal salts with olefins are less stable; thus $K_p = 0.33$ litre mol^{-1} and $-\Delta H = 6$ kJ mol^{-1} (at 298 K) for the complex of $TiCl_4$ with isoprene[157].

Metal halides can form complexes with the majority of organic solvents[158].

Thus a wide variety of complex formation processes occur in hydrogen chloride–unsaturated compounds–catalyst–solvent systems. The most important of these are the formation of a complex by hydrogen chloride with olefins and also by the catalyst with olefins and hydrogen chloride. In concentrated solutions in non-polar media hydrogen chloride is to a large extent associated. Without studying these processes, a correct treatment of kinetic data is impossible. Complex formation is a characteristic feature of the systems considered and must be taken into account in the study of the mechanism of the hydrochlorination reaction. Complexes in which there is a significant rearrangement of the electronic structure of the molecule and comparatively strong intermolecular bonds are formed are the most important for the reaction.

V. THE MECHANISM OF THE ADDITION OF HYDROGEN CHLORIDE TO MULTIPLE BONDS

The hydrochlorination reactions can proceed via radical and molecular mechanisms. The radical addition of hydrogen chloride takes place slowly and fairly rarely[30,159–162]. This

pathway is not characteristic of hydrochlorination. The ionic and molecular mechanisms are much more important.

1. The Ionic Mechanism of Hydrochlorination

(a) *Evidence for the involvement of ions in the reaction.* The idea of the involvement of ions or ion pairs in hydrochlorination is based mainly on the results of the study of the composition of the addition products. The validity of the Markovnikov rule is typical for ionic processes; it is based on the tendency of the proton to attack the sites with the highest electron density at the C–H bonds in the olefin molecule[35]. The modern interpretation of the Markovnikov rule is based on the rapid rearrangement of primary alkyl cations to the more stable secondary cations:

$$RCH=CH_2 \xrightarrow[-Cl^-]{HCl} \left[\begin{array}{l} \longrightarrow RCH_2CH_2^+ \\ \longrightarrow RCH^+CH_3 \end{array} \right] \xrightarrow{\text{just}} \quad .$$

Quantum-mechanical calculations, including non-empirical calculations, predict that the primary cations of the type $CH_3CH_2CH_2^+$ or $ClCH_2CH_2^+$ are unstable and cannot exist under the usual conditions. They should be converted without activation energy into the more stable cations $CH_3CH^+CH_3$ or $ClCH^+CH_3$.[163] Thus the protonation is thermodynamically controlled and the Markovnikov rule can be explained within the framework of an ionic mechanism.

The involvement of ions in the hydrochlorination in hydroxylated solvents explains the simultaneous formation of solvent addition products. The carbonium ions formed in the reaction are subjected to nucleophilic attack not only by Cl^- anions but also by solvent molecules:

$$RCH=CH_2 \xrightarrow[-Cl^-]{HCl} RCH^+CH_3 \left[\begin{array}{l} \xrightarrow{Cl^-} RCHClCH_3 \\ \xrightarrow[-H^+]{R'OH} RCHCCH_3 \\ \qquad\quad | \\ \qquad\quad OR' \end{array} \right] .$$

The rearrangements of branched olefins can be attributed to rapid isomerisation reactions of the carbonium ions:

$$(CH_3)_2CHCH=CH_2 \xrightarrow[-Cl^-]{HCl} (CH_3)_2CHCH^+CH_3 \xrightarrow{\text{just}} (CH_3)_2C^+CH_2CH_3$$
$$\downarrow Cl^- \qquad\qquad \downarrow Cl^-$$
$$(CH_3)_2CHCHClCH_3 \qquad (CH_3)_2CClCH_2CH_3 \ .$$

The involvement of ionic species in a catalytic process is believed to be confirmed by the exchange of the halogen between HCl and the catalyst, which has been observed in the hydrochlorination of styrene[79]:

$$C_6H_5CH=CH_2 + HCl + SnBr_4 \rightarrow C_6H_5CH^+CH_3SnBr_4Cl^- \left[\begin{array}{l} \longrightarrow C_6H_5CHClCH_3 \ ; \\ \longrightarrow C_6H_5CHBrCH_3 \ . \end{array} \right.$$

The acceleration of hydrochlorination in polar media and also the isotope effect in the reaction close to unity, indicating that the H–Cl bond is broken in the transition state, are consistent with the ionic character of the process.

In the ionic mechanism, the hydrochlorination is treated as a stepwise process consisting of a sequence of ion or ion pair formation reactions and the addition of a nucleophilic species. According to a number of workers[1], ionisation is preceded by the formation of complexes of HCl with the unsaturated compound or the catalyst.

In the simplest case the reaction can be represented schematically as follows:

$$RH + HCl \ (\text{or } RH \cdot HCl) \underset{(a)}{\rightarrow} RHH^+Cl^- \underset{(b)}{\rightarrow} RH_2Cl \ .$$

Processes which are the reverse of reactions (*a*) do not play a significant role in hydrohalogenation, since there is no isotope exchange between olefins and deuterium halides[22,56,164]. 1,2-Dimethylcyclohexene, where the migration of the double bond indicates the reversibility of the ionisation stage, constitutes an exception[72].

(b) *The ionisation stage.* The accumulation of measurable amounts of ionised species has not been observed in hydrochlorination. Inductive periods on the product accumulation curves are not characteristic of hydrochlorination either. This suggests that the formation of ionic species is the rate-limiting stage of the reaction. Only reactions in aqueous media, where the degree of dissociation of HCl into ions is high, may be exceptions.

Ions can arise in the reaction system as a result of the interaction of Cl with the unsaturated compound or after the preliminary dissociation of HCl and the reactions of the resulting ions with the multiple bonds. The majority of organic compounds have proton affinities in the range 500 to 800 kJ mol^{-1}.[165] Ions of the protonated solvent should be formed in solution. The degree of dissociation of HCl in organic solvents is low and is usually in the range 10^{-3} to 10^{-10}%.[19,25,104,166] The dissociation is facilitated by the interaction with a second HCl molecule and the formation of the HCl_2^- ion. The dimer $(HCl)_2$ is a stronger acid than HCl. Thus the dissociation of HCl in an organic solvent(Solv) can be represented schematically as follows:

$$Solv + (HCl)_2 \underset{}{\overset{K_{(HCl)_2}}{\rightleftarrows}} Solv\,H^+ + HCl_2^- \quad (\text{or } Solv + 2HCl \rightleftarrows Solv\,H^+ + HCl_2^-) \ .$$

This process is significant if the bond between the proton and the solvent is stronger than that between the proton and the unsaturated compound. For reactions in hydrocarbons and halogeno-derivatives, whose proton affinity is lower than that of olefins, preliminary ionisation is unimportant. It plays a major role in oxygen-containing solvents such as nitromethane, ethers, and carboxylic acids, whose proton affinities are comparable with those of olefins[165]. However, in this case the hypothesis of preliminary ionisation is inconsistent with the frequently observed second order of the reaction with respect to hydrogen chloride. If the rate of reaction were proportional to the concentration of the ions [Solv H^+] formed in the preliminary stage, defined by the expression

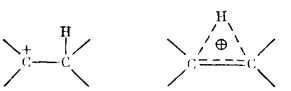
$$[Solv\,H^+] = \sqrt{K_{(HCl)_2}[HCl]^2[Solv]} = [HCl]\sqrt{K_{(HCl)_2}[Solv]} \ ,$$

subject to the condition [Solv H^+] $\ll$ [HCl], then the order of the reaction with respect to HCl should not exceed unity.

Thus the most probable pathway leading to the formation of ions in the reaction is the interaction of hydrogen chloride with the unsaturated compounds.

An ion pair can arise either directly on collision of the molecules or on decomposition of the complex of the unsaturated compound with one or several HCl molecules. These two pathways are kinetically indistinguishable. The enthalpies of formation of the complexes of HCl with olefins are much lower than the activation energy for hydrochlorination and complex formation does not therefore influence significantly the rate of ionisation.

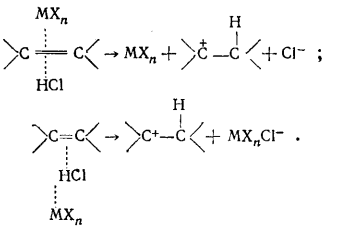
Ionisation results in the formation of an ion pair consisting of the carbonium ion and the HCl_2^- or Cl^- anion. These cations can have the classical (open-chain) or bridged structure:



Quantum-mechanical calculations indicate a greater stability of the bridged structure in the case of the $C_2H_5^+$ ion and approximately equal bond energies for the two structures of the vinyl cation $C_2H_3^+$.[163] In solutions the relative stabilities

of the two forms of the cations are determined by their solvation energies. Delocalisation of the charge diminishes this energy and for this reason in solution the stability of the ion with the classical structure increases. This structure of the carbonium ion is indicated by the high yield of the products of *cis*-addition in many hydrochlorination processes.

In the presence of a catalyst the transition state contains at least three molecules. Their interaction can occur in the following ways:



In the second case the formation of an ion pair is facilitated by the interaction of the catalyst MX_n with the anion Cl^- and this pathway appears to be the most probable.

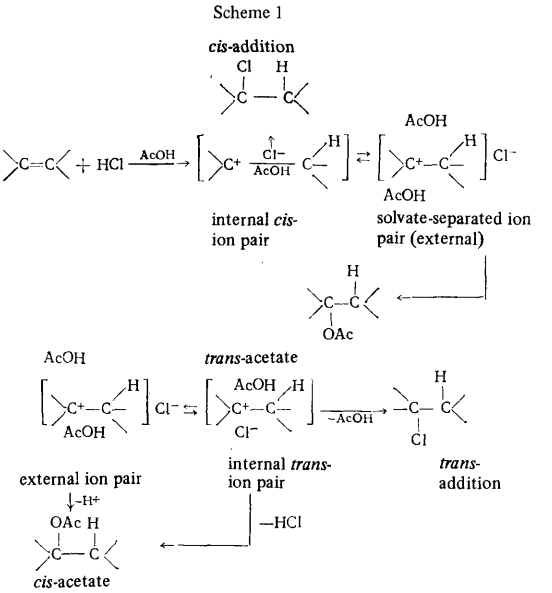
The formation of a stable complex of the olefin with the catalyst should not promote hydrochlorination. Indeed, the binding of $AlCl_3$ in a complex with an excess of the olefin inhibits the hydrochlorination and gives rise to side processes[103,104]. However, in the hydrochlorination of acetylene the catalytic activity of metal halides is correlated with the stabilities of the corresponding complexes of acetylene, which is due to the formation of ternary complexes[167]. The involvement of such complexes in the process is consistent with the molecular mechanism of hydrochlorination and is considered below in Section V.

According to Velichko-Shkurchenko[104] and Flid[106], in catalytic hydrochlorination ionisation precedes the formation of the complex acids $HMCl_{n+1}$ and ternary complexes involving the olefin. In certain cases the kinetic data demonstrate the simultaneous involvement of two olefin molecules in the ionisation stage[106].

(c) *The reaction product formation stage.* The hydrochlorination products are apparently formed directly from the ion pair[2,69,72]. This claim is based on the high (up to 100%) yields of the *cis*-addition products. The involvement in the process of the free open-chain ion, where there is a possibility of hindered rotation, should lead to identical amounts of the *cis*- and *trans*-products, which happens for a number of hydrochlorination reactions in highly polar media. For the bridged cation, preferential *trans*-addition is to be expected. *cis*-Addition is possible only for the ion pair[168], which agrees with the thermodynamics of the dissociation process. In solvents with $\varepsilon < 15$, the dissociation of the ion pair into singly charged ions requires an expenditure of up to 200 kJ mol^{-1} of energy and this process should not take place to an appreciable extent in media of moderate polarity[169].

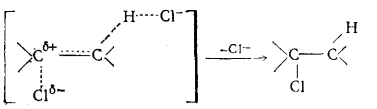
The conversion of ion pairs into reaction products can be considered within the framework of the competition between two mechanisms—the bimolecular Ad_{E^2} mechanism and the termolecular Ad_{E^3} mechanism[56,66,72,85]. The Ad_{E^2} mechanism describes the reaction of the ion pair obtained from the unsaturated compound and HCl. It is also applicable to a third-order reaction if the HCl_2^- anion is involved in it. The bimolecular process mechanism is presented below (Scheme 1) in relation to the interaction of the olefin with HCl in acetic acid[66]:

Scheme 1



Scheme 1 explains satisfactorily the formation of the *cis*- and *trans*-products of the addition of hydrogen chloride and the solvent. For 3,3-dimethylbutene, the ion pair is rapidly converted into the products; the ions external in relation to the ion pair cannot influence the formation of the products and the addition of salts and a change in the concentration of HCl do not affect their composition. The increase of the stability of the ion pair on passing to styrene increases the selectivity of the reaction: the ratio of the yields of the chloro-derivative and the acetate increases[56]. The Ad_{E^2} mechanism is characteristic of hydrochlorination at an insignificant concentration of the Cl^- anion; the occurrence of the reaction via this mechanism is promoted by an increase of temperature and the possibility of the delocalisation of the positive charge on the cation[85].

The termolecular mechanism is significant at high HCl concentrations or in the presence of additives of the type of $(CH_3)_4NCl$.[56,85,170] The transition state in Ad_{E^3} process can be represented as follows:



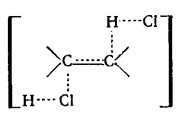
cis-Addition via this mechanism should be sterically hindered. The synchronous dissociation of the H–Cl bond and the formation of two new bonds and the delocalisation of the change in the transition state decrease the activation barrier to the reaction relative to the bimolecular process. A decrease of temperature promotes the occurrence of the reaction via the Ad_{E^3} mechanism. A similar Ad_{E^3} mechanism was first proposed for the addition of acids to acetylene derivatives in ionising media in the presence of LiCl as early as the 1950's.[171,172]

The presence of the Cl^- or HCl_2^- anions is of decisive importance in the termolecular process. The Ad_{E^3} mechanism explains satisfactorily the *trans*-stereospecificity of many hydrochlorination reactions under specific conditions. Addition via the Ad_{E^3} mechanism takes place in the absence of additives in the case of cyclohexene[71,170] and alkylacetylenes[85]. Highly polar and strongly ionising solvents tend to

increase the concentration of Cl^- anions and favour the Ad_{E^3} addition. The increase of the yield of the *trans*-product of hydrochlorination on passing from acetyl chloride to acetic acid and methanol is attributed to this[72]. The relative contributions of the bimolecular and termolecular mechanisms of ionic hydrochlorination depend on the choice of solvent and on the structure of the initial compound.

Thus the ionic mechanism of hydrochlorination with allowance for the competition between the Ad_{E^2} and Ad_{E^3} processes explains satisfactorily the characteristics of the reactions in strongly polar and hydroxylated solvents. Many characteristic features of the hydrochlorination in weakly polar media are inconsistent with the hypothesis of the involvement of ionic species in the reaction.

According to the ionic mechanism of addition in non-polar solvents of the type of pentane, the Ad_{E^2} pathway should operate with formation of the *cis*-hydrochlorination product. However, Table 2 shows that *trans*-addition is characteristic of many reactions in pentane. This is attributed to the fact that the hydrochlorination takes place by a synchronous mechanism with participation of two hydrogen chloride molecules via the transition state[70]



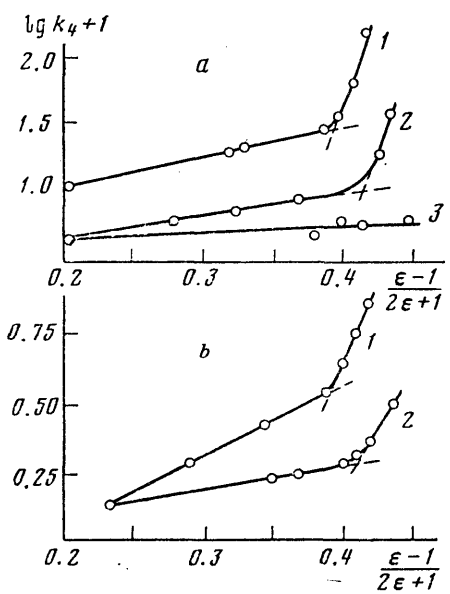


Figure 3. Dependence of the logarithm of the rate constant for the hydrochlorination of cyclohexene on the dielectric constant of the medium ε in terms of the Kirkwood variables at different temperatures (K): *1*) 293; *2*) 253; *3*) 183; *a*) C_6H_{14}–CH_2Cl_2; *b*) CCl_4–CH_2Cl_2.[6,109]

It is impossible to classify such a reaction as rigorously ionic, since the product is not formed via the ions but simultaneously with the formation of the latter. It has already been mentioned that the appearance of free ions in non-polar solvents requires a large expenditure of energy, while the hydrochlorination reaction in such media is characterised by a low activation energy. Thus it is not possible to account for the stereochemistry of the addition of hydrogen chloride in non-polar media from the standpoint of the ionic mechanism.

Nor does the ionic mechanism explain the fact that in many instances where the protonation of different olefins yields the same cation the products of the hydrochlorination of these olefins are different[46,93,173].

If the rate of the ionic process is limited by the ionisation stage, one must expect the acceleration of hydrochlorination on passing to polar solvents. In reality the increase of the rate of reaction with increasing polarity is frequently slight or does not occur at all. The ionic mechanism is not consistent with the kinetic isotope effect in the hydrochlorination of cyclohexene in hexane in the presence of $SnCl_4$.[110]

Estimation of the degree of charge separation in the transition state of the hydrochlorination reaction indicates the absence of ions from weakly polar media. For processes with a rate-limiting ionisation stage of the type of the solvolysis of alkyl halides and acid chloride or the Menshutkin reaction, the degree of charge separation $q^{\neq}$ is in the range 0.7–1.0 of an electronic charge unit[174]. Fig.3 illustrates the dependence of the rate of catalytic hydrochlorination of cyclohexene in terms of the Kirkwood variables on the polarity of the medium[6,109]. At temperatures in the range 253–293 K for media with dielectric constants below 6–8, $q^{\neq}$ is small and amounts to 0.2–0.4. At 183 K, $q^{\neq}$ does not exceed 0.3 over the entire range of dielectric constants $\varepsilon < 16$. The values $q^{\neq} \cong 0.5$–0.9, corresponding to an ionic reaction, have been obtained at 253–293 K in media of moderate polarity ($6 < \varepsilon < 12$).

Thus the ionic mechanism is unsuitable for the description of hydrochlorination in weakly polar media, particularly at low temperatures. The characteristic features of such reactions can be accounted for by a molecular mechanism, which is probable also for gas-phase processes where there are no solvation effects stabilising ions or ion pairs.

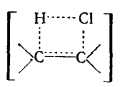
2. The Molecular Mechanism of Hydrochlorination

The molecular mechanism of hydrochlorination presupposes the formation of the addition product via a synchronous rearrangement of the bonds in the reactant molecules without their preliminary dissociation into ions or radicals. The energy consumed in the dissociation of old bonds is compensated by the energy of formation of new bonds. The synchronous rearrangement without dissociation takes place when the molecules in the transition state form a ring incorporating the carbon atoms of the double bond and one or several molecules of hydrogen chloride.

The energy of formation of the cyclic transition state from the molecules A and D is determined, according to modern ideas, primarily by the form of the potential curves for the ground and lowest excited configurations of the reacting system[175]. In those cases where the reactant molecules do not exhibit distinct electron-donating and electron-accepting properties, the excited configuration with charge transfer $D^+ A^-$ has a high energy and does not play a significant role in the formation of the transition state. Low activation energies may be observed if the ionisation potential I_D is relatively low and the electron affinity of the molecule A is high, i.e. under the conditions of a strong donor–acceptor interaction. In the reaction system considered, such interaction occurs, for example, on formation of complexes of

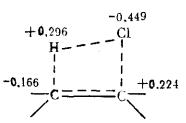
hydrogen chloride with unsaturated compounds. The formation of a cyclic transition state with a low energy in the HCl–olefin system is therefore possible. Four-membered and six-membered transition states are the most likely. The second and third orders of the reaction correspond to the four-membered and six-membered transition states respectively.

(a) *Second-order reactions with a four-membered transition state.* The addition to multiple bonds via a cyclic transition state of the type



has been considered in the literature before the appearance of the hypothesis that carbonium ions are involved in the reaction. Interest in such processes arose again after the publication of a study[14] in which the characteristics of the hydrohalogenation of olefins in the gas phase were accounted for by the involvement of the so called semi-ion pairs. In these pairs the reactant molecules are polarised and the charge on the hydrogen atom and one of the carbon atoms is +0.5, while that on the chlorine atom and the other carbon atom is −0.5. The energy of formation of ion pairs in the gas phase exceed significantly the observed activation energies for the addition reactions and the hypothesis of the polarisation of the molecules in the transition state and not their ionisation was therefore put forward. This hypothesis explained the validity of the Markovnikov rule and the correlation of the reactivities of olefins with their ionisation potentials. The choice of a charge of 0.5 is arbitrary, but calculation of the energies of formation of four-membered rings, where the molecules are polarised in this way, agrees satisfactorily with the activation energies for the gas-phase addition and elimination reactions. The proposed model agrees in the main with the results of semiempirical quantum-mechanical calculations[176].

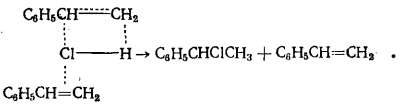
It has been suggested recently that the transition state be regarded as an asymmetric ring[177]. The quantum-mechanical calculation on the transition state in the ethylene–hydrogen chloride system by the INDO/3 method leads to a similar structure[128], for which the following charge distribution in the ring was obtained:



The asymmetric charge distribution leads to the large dipole moment $\mu^{\neq} = 2.88$ D. The overall charge on the HCl molecule is −0.153, which indicates charge transfer from ethylene to hydrogen chloride. The results obtained in the above study[128] agree better with the donor–acceptor properties of the reacting molecule than the hypotheses developed previously[14].

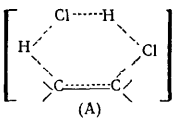
The agreement between the molecular mechanism of addition via a four-membered transition state and the orbital symmetry rules has been considered in a monograph[175] and in another publication[178]. It was shown that, in the presence of an appreciable charge transfer in the asymmetric transition state, molecular addition via a four-membered ring is possible.

The molecular mechanism with a four-membered transition state in the gas phase has been adequately proved. The possibility of a similar reaction in the liquid phase has been postulated[69,85], but so far this problem has not been analysed in detail and preference has been given to the traditional ionic mechanism. For the hydrochlorination of styrene, the following structure of the four-membered transition state, stabilised by a second styrene molecule, has been postulated[179]:



Although adequate confirmation of this mechanism has not been obtained, one cannot rule out the possibility of the stabilisation of cyclic structures by the molecules of olefins or other organic donors. For example, the characteristics of the hydrobromination reaction, which resembles the hydrochlorination process, in the absence of radical initiators can be explained, if it is assumed that the anomalous addition product is formed via a four-membered cyclic transition state stabilised by a second olefin molecule[5].

(b) *Higher-order reactions with a six-membered transition state.* The hydrochlorination products can be obtained via a synchronous rearrangement of the bonds in the six-membered ring formed by two molecules of hydrogen chloride and the double bond of the unsaturated compound:



(A)

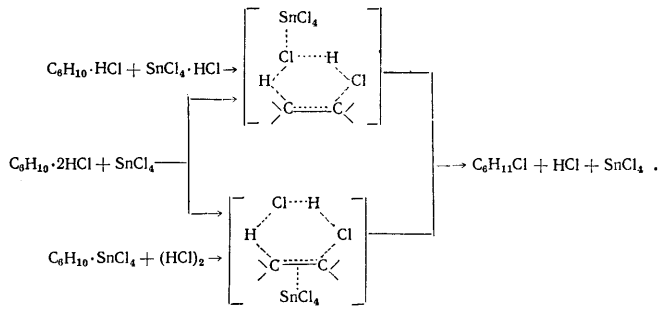
Addition via such a transition state has been demonstrated for the Diels–Alder reaction[180] and also for the exchange of atoms between the molecules of mixed halogens and their dimers[181] in the gas phase. This mechanism is most probable for bromination[182] and hydrobromination[5] in non-polar media. The above reactions are characterised by high negative activation entropies, low or negative activation energies, and a weak dependence of the rate of reaction on the polarity of the medium. The characteristics enumerated above are observed also in the hydrochlorination of many olefins in non-polar and weakly polar media. Large negative activation entropies are associated with the formation of highly oriented cyclic structures in which the gain in the free energy of activation is compensated by the decrease of the energy of the transition state as a result of the increase of the strength of the donor–acceptor bonds and the delocalisation of the electron density in the ring.

Six-membered cyclic transition states in hydrohalogenation were first proposed by Shilov to account for the *cis*-stereospecificity of the addition of HBr to acetylene derivatives[183]. According to the results of Smirnov-Zamkov and Piskovitina[184], the *trans*-addition of HBr to cyclohexene is also consistent with the molecular six-centre mechanism if account is taken of the steric disposition of the bonds in the cyclohexane molecule. The stereochemistry of the addition cannot serve as adequate evidence for or against the molecular mechanism. Our analysis[108] of the transition state in hydrochlorination reactions on molecular models showed that, under the conditions of a slight extension of the H–Cl bonds, a six-membered ring can be constructed for both *cis*- and *trans*-addition. The *trans*-pathway of the addition reaction does not therefore justify the rejection of the molecular mechanism as has been done by some investigators[75,168].

The formation of a six-membered transition state with a relatively low activation energy explains the finding that at room temperature HCl adds to olefins in the gas phase at a rate higher by many orders of magnitude than would follow from the extrapolation of the kinetic data for the high-temperature process[89]. The interaction of the transition state

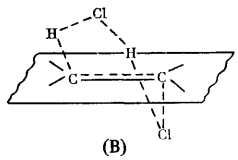
with a third hydrogen chloride molecule can lower the energy of the system. This mechanism appears to be the most likely for gas-phase reactions at room and reduced temperatures.

A molecular mechanism of a catalytic liquid-phase reaction has been proposed for the hydrochlorination of cyclohexene[6] in view of the low degree of charge separation in the transition state and the second order of the reaction with respect to hydrogen chloride. The reaction products can be formed via the following mechanism:



The transition states in the reactions have the same compositions but different structures and correspond to different stereochemistries of the addition. The nearly zero process activation energies in non-polar media at low temperatures and high (230–270 J mol^{-1} K^{-1}) negative activation energies as well as the appreciable isotope effect in the reaction of hexane are consistent with the molecular mechanism[6,108–110].

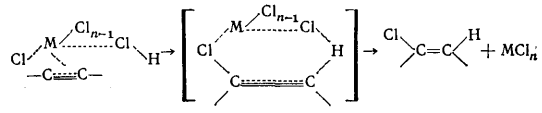
The orientation in the transition state is determined by the nature of the unsaturated compound. For the majority of olefins, the nearly planar structure (A) is more probable. Structure (B), which leads to the formation of the *trans*-addition product, may be more favourable for cyclic compounds:



(B)

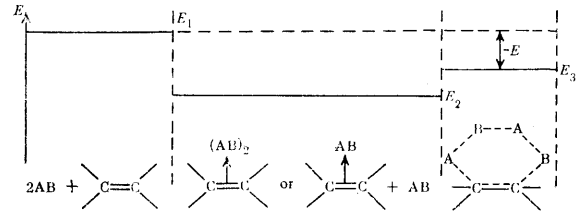
Lewis acids facilitate the reaction by stabilising the cyclic transition state. The catalyst can interact with a hydrogen chloride or olefin molecule. Both types of complex formation are accompanied by an energy gain; in the hydrochorination of cyclohexene in the presence of $SnCl_4$, the interaction of the catalyst with hydrogen chloride is more favourable.

Another six-membered transition state, incorporating in the ring the molecules of the unsaturated compound, hydrogen chloride, and the catalyst, has been proposed for the catalytic hydrochlorination of acetylenic derivatives[167]. The transition state of the process has a structure intermediate between a ternary complex of the starting materials and the reaction products:



This mechanism can be due to the ability of acetylenic compounds to form carbon–metal bonds and appears less likely for olefins. The absence of halogen exchange in the products of the hydrochlorination of cyclohexene in the presence of $SnBr_4$ at low temperatures rules out the formation of such a transition state[110]. At higher temperatures cyclohexyl bromide is formed in the reaction (after an inductive period). If the cyclic transition state incorporated a catalyst molecule, the bromide should have been obtained with a high yield simultaneously with the chloride, which has not been observed in a non-polar solvent.

High-order molecular reactions are characterised by low or negative activation energies E, which can be explained by the contribution of the heats of reversible intermediate stages, including complex formation[7], where the energy of formation of the cyclic transition state from the complexes is low and the energy level of this states lies below that of the initial molecules. The addition of the reactant AB to the double bond can be illustrated schematically in the following manner:



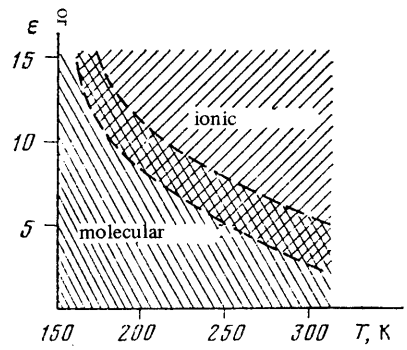


Figure 4. Schematic illustration of the preferential operation of different mechanisms of the hydrochlorination of cyclohexene in the presence of $SnCl_4$ as a function of the process conditions.

In this case E is determined by the expression $E = E_3 - E_1 < 0$. At high concentrations and low temperatures, the degree of binding in the complex is close to 100% and it is then to be expected that $E = E_3 - E_2 > 0$. A negative temperature coefficient, associated with the complex formation, is possible only when the complex lies on the reaction coordinate. If other causes of this phenomenon have been ruled out, then a negative activation energy serves as a criterion of the involvement of the complex in the process[7,182].

It is at present still difficult to formulate sufficiently unambiguous conditions for the occurrence of hydrochlorination via the molecular mechanism. The majority of the characteristic features of the processes in the gas phase and in non-polar solvents agree better with the molecular mechanism than with the ionic mechanism. The ionic mechanism has been demonstrated for reactions in highly polar and

hydroxylated media. In solvents with a moderate solvating capacity a transition from one mechanism to another is to be expected. A change in mechanism has been observed in the catalytic hydrochlorination of cyclohexene by noting the sharp breaks in the linear plots in terms of the Kirkwood variables (Fig.3) and has been confirmed by other data[6,110]. At room temperature the transition from the molecular to the ionic mechanism occurs even in the range of dielectric constants from 4 to 6. A decrease of temperature extends the region in which the molecular mechanism operates and at 183 K the majority of the features typical for the molecular pathway are observed even for $\varepsilon > 10$. Fig.4 illustrates the regions of the operation of the two mechanisms of the addition of hydrogen chloride in relation to the catalytic hydrochlorination of cyclohexene. Presumably the presence of substituents at the double bond stabilising the carbonium ion and also the introduction of Lewis acids stronger than $SnCl_4$ increase the region where the ionic mechanism operates.

The mechanism of hydrochlorination in frozen hydrogen chloride–olefin systems is of great interest. Reactive olefins such as isobutene react rapidly with hydrogen chloride below the melting point[12]. Presumably, as in the liquid phase, at low temperatures the solid-phase process takes place via the molecular mechanism.

* * *

The data on the product composition and the kinetics of the spontaneous and catalytic hydrochlorination show that the process proceeds via two mechanisms: ionic and molecular. Considerable activation energies and low activation entropies, a marked dependence of the reaction rate on the polarity of the medium, a high degree of charge separation in the transition state, the absence of an isotope effect in the reaction, and the formation of mixed addition products are characteristic of the ionic process. Zero or negative activation energies, high negative activation entropies, a weak dependence of the rate on the dielectric constant of the medium, the presence of an isotope effect, and the absence of mixed addition correspond to the molecular mechanism.

There is no reason to treat these mechanisms as mutually exclusive. They can operate simultaneously and have features in common. Thus ionisation can proceed via cyclic transition states characteristic of the molecular pathway and the energy expended on the formation of ions may be compensated by the energy of the C–H and C–Cl bonds formed. This mechanism may be called molecular-ionic. A molecular reaction without the participation of ions is characterised by a considerable charge separation. There apparently exist a whole series of intermediate cases between purely ionic and purely molecular reaction pathways.

The ideas which we have described differ from those in the scientific and monograph literature familiar to the majority of chemists. The new approach to the mechanism of the classical addition reaction became possible as a result of the development of kinetic studies, the application of modern experimental techniques, and the expansion of the range of experimental conditions. Further studies in this field will introduce additional revisions to the ideas being developed. The hydrochlorination reaction is not exceptional. The application of modern physicochemical methods in the study of the kinetics and intermolecular interactions, the expansion of the temperature and reactant concentration ranges, and the use of the results of quantum-mechanical calculations will undoubtedly lead to a significant revision of the traditional ideas concerning the mechanisms of many processes.

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