Role of water traces in the liquid-phase catalytic hydrochlorination of olefins in organic solvents

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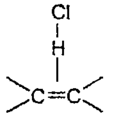
The liquid-phase hydrochlorination of 4,5,6,7,8,8,-hexachloro-3',4,7,7'-tetrahydro-4,7-methanoindene (Chlordene) catalyzed by gallium or aluminum halides occurs in the presence of water traces in an aprotic organic solvent. Complexes $H_2O \cdot M_2X_6$, where M is metal and X is halogen, catalyze this reaction. The reaction proceeds under homogeneous conditions. Under heterogeneous catalytic conditions, the solid phase in the $AlCl_3$—CCl_4 system attains the required concentration of $AlCl_3$ in the solution. It was shown using quantum-chemical PM3 calculations that the water molecule facilitates the transfer of proton in the form of the hydroxonium ion from an HCl molecule to olefin.

Key words: hydrochlorination, olefins, catalysis, complex, water, aluminum and gallium halides, PM3.

It is commonly believed[1] that at the first stage of hydrochlorination of olefins an unstable compound is formed due to the interaction of the electrophilic reagent with π-electrons of the double bond of olefin (π-complex **1**).



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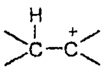

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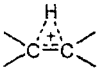

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At the second stage, the π-complex is transformed into a carbonium ion, which can have the structure of a classic (**2**) or bridged (**3**) carbocation. Nucleophilic attack by the chloride ion on the complex formed is the third stage.

Any catalyst for the hydrohalogenation of unsaturated compounds is assumed to serve[2] first of all for the polarization of an HHal molecule due to the donor-acceptor interaction. The donor-acceptor bond is formed between the Hal atom of the HHal molecule and the catalyst, and the hydrogen bond is a particular case. This is accompanied by an additional transfer of the electron density from the H atom of the HHal molecule to the catalyst. The role of the catalyst is also manifested in changes in steric and solvation effects. This can explain the catalytic effect of water described previously.[3—5] Dimers and trimers of HCl can also be considered as catalytic complexes. This assumption can explain the second and third orders with respect to HCl in kinetic equations, indicating that the degree of association of HCl in a solvent should be taken into account.[5,6]

The Lewis acids ($AlCl_3$, $FeCl_3$, $SnCl_4$, and $ZnCl_2$) are widely used as the catalysts for hydrochlorination. It is believed that the first stage of the reaction results in the formation of the complex acid $H^+[MCl_n]^-$, which is stronger than HCl and serves as a proton donor.[7—9] The Lewis acids are strong σ-acceptors; therefore, admixtures that form complexes with metal halides can affect the reaction. Water is a strong n-donor, whose traces are almost always present in the reaction mixtures.

In this work, we studied the effect of water traces on the liquid-phase catalytic hydrochlorination of olefins using as an example the hydrochlorination of 4,5,6,7,8,8-hexachloro-3',4,7,7'-tetrahydro-4,7-methanoindene (Chlordene) catalyzed by aluminum and gallium halides.

Experimental

Aluminum chloride (chemically pure grade) was purified by double sublimation *in vacuo* with NaCl. Hydrogen chloride (chemically pure grade) was dehydrated by passing through concentrated H_2SO_4. In the experiment with a minimum content of water in the system, HCl was additionally purged through a column with molecular sieves 4A. Chlordene was obtained by condensation of hexachlorocyclopentadiene with cyclopentadiene in a solution of anhydrous CCl_4 with addition of hydroquinone at temperature <60 °C followed by repeated recrystallization from ethanol. The purity of the product was monitored by m.p. (166—167 °C) and TLC data. Cyclohexane

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(chemically pure grade) was purified by refluxing with sodium followed by distillation (the water content was not greater than $3 \cdot 10^{-4}$ wt.%). Carbon tetrachloride (chemically pure grade) was dehydrated over $CaCl_2$, distilled, and additionally dehydrated with molecular sieves 4A (the water content was not greater than $7 \cdot 10^{-4}$ wt.%). 1,2-Dichloroethane (DCE) (chemically pure grade) was dehydrated with $CaCl_2$ and distilled (the content of water in the purified solvent was not greater than $33 \cdot 10^{-4}$ wt.%). The content of water in CCl_4 was determined by IR spectroscopy on a Specord-80M spectrometer in a cell with BaF_2 windows (thickness 10 cm, ν = 3712 cm^{-1}, ε = 9.6)[10] and in DCE and cyclohexane by potentiometric titration (Fischer's method) on a Ridan instrument. All experiments were carried out in an atmosphere of anhydrous argon. The content of $AlCl_3$ in a solution of the catalytic complex was determined by the standard procedure of complexonometric titration. The IR spectra of the reaction mixtures were recorded on a Perkin—Elmer 580 spectrometer.

Procedure of Chlordene hydrochlorination under heterogeneous conditions. A solvent (with different water contents) was placed in a reactor, and weighed samples of Chlordene and $AlCl_3$ were introduced with stirring. The reaction was carried out to completion in the same reactor with bubbling anhydrous HCl.

Procedure of Chlordene hydrochlorination under homogeneous conditions. The catalytic complex was prepared by the method described for heterogeneous catalysis, and HCl was purged through the reaction mixture for 3 min (time sufficient for the appearance of color in all experiments). The mixer was stopped, the reaction mixture was stored during 1 h, and the liquid phase was carefully decanted to the hydrochlorination reactor, taking a sample to determine the content of $AlCl_3$, Chlorodene, and Dilor in the solution. Portions of the solvent with different water contents (to change the H_2O : $AlCl_3$ ratio) were added with stirring to the liquid phase in the hydrochlorination reactor from the reactor for preparing the catalytic complex, the weighed samples of Chlordene were introduced, and HCl was fed. The amounts of the components added were determined from the condition that the volume of the reaction mixture and the initial concentration of Chlordene remained unchanged in all experiments.

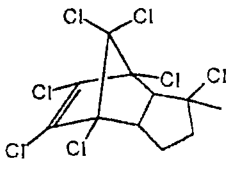
When $GaCl_3$ was used as the catalyst, the solvent was placed in the hydrochlorination reactor, weighed amounts of $GaCl_3$ and water were added with stirring, a weighed sample of Chlordene was introduced, and HCl was fed.

Calculations were performed by the semiempirical PM3 method[11] using the MOPAC program[12] with full optimization of the geometric parameters.

Results and Discussion

The liquid-phase hydrochlorination of Chlordene in the presence of the III Group metal halides in aprotic solvents (CCl_4, DCE, cyclohexane) results in the formation of the 2-exo-isomer (β-Dilor), which possesses pesticide properties.

The conditions of the reaction in the kinetic region were determined in preliminary experiments, and the order of introducing the reagents was shown to have no effect on the reaction course. Aluminum chloride is insoluble in any of the solvents mentioned, while $AlBr_3$ and $GaCl_3$ are soluble in DCE and cyclohexane.[13]



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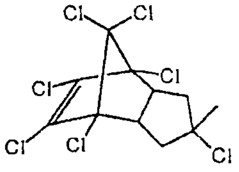

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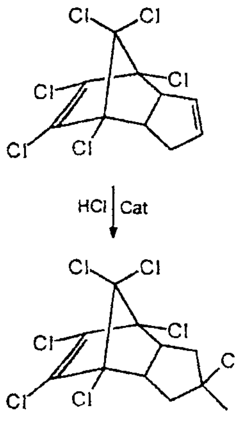

β-Dilor

As established by GLC, both halides exhibit almost the same catalytic activity in the Chlordene—HCl—AlX_3—CCl_4 systems (where X = Cl, Br). The IR spectra (CCl_4) of the reaction mixture contained, along with bands of the reagents and reaction products, new bands at 1490, 1484, 1312, 1214, 1165, and 937 cm^{-1}, and the intensity of bands at 1444, 1075, 1061, and 1037 cm^{-1} increased. A similar appearance of new bands and a sharp change in the intensity in the 1500—1000 cm^{-1} region were observed in the IR spectra of arenonium ions.[14]

Arenonium ions are usually viscous oils or low-melting solids with color from light-yellow to red.[14] Reaction mixtures of the systems under study are colored, and the color is observed only when all of the four components are present: olefin, HCl, the Lewis acid, and a solvent; when at least one of these components is absent, the solution is colorless. The reaction product is formed only after the reaction mixture gains color, *i.e.*, the formation of the colored complex is most likely an intermediate stage of the reaction. When the reaction occurs in CCl_4 or cyclohexane, these colored complexes are formed as an oil, which soon loses its color in air. When DCE is used as the solvent, no oil is formed, which is probably related to the fact that the specific solvation of the complex in DCE is higher than in CCl_4.

It was established for the reaction with crystalline $AlCl_3$ under heterogeneous conditions that the poor reproducibility of data is due to the dual effect of water: a small amount of water catalyzes the reaction, and a great amount of water results in the inhibition due to hydrolysis of the Lewis acid ($AlCl_3$), whose products, as shown previously, do not catalyze the reaction. However, the effect of even a small amount of water is unambiguous. No reaction product is formed when water is absent and $AlCl_3$ of high purity grade is used. The addition of water results in the appearance of color and the formation of the reaction product.

Since $AlCl_3$ is insoluble in any of the solvents used, the reaction occurs either *via* the adsorption mechanism or a portion of $AlCl_3$ is transferred to the solution due to the complex formation, and the reaction proceeds in the homogeneous phase. In the last case, $AlCl_3$ should be observed in the liquid phase. This was confirmed by the complexonometric titration. Regardless of the ratio of the components added, in all experiments the ratio of concentrations of H_2O and $AlCl_3$ dissolved in the reaction mixture is equal to 1 : 2.

When the reaction was carried out under the homogeneous conditions in the $AlBr_3$—cyclohexane and $GaCl_3$—DCE systems, the reaction mixture was also colored, and the formation of Dilor was detected by GLC. Therefore, the hydrochlorination can be performed under homogeneous conditions. Evidently, maintaining a required concentration of $AlCl_3$ in the solution is the only role of the solid phase in the $AlCl_3$—CCl_4 system used in industry.

Under homogeneous catalytic conditions, the effect of water was studied in a medium of CCl_4 and DCE. When $AlCl_3$ was used as the catalyst, the catalytic complex was preliminarily obtained in a special reactor under heterogeneous conditions (see Experimental). The dissolved catalytic complex of $GaCl_3$ with H_2O was prepared directly in the reactor for hydrochlorination.

The results of the hydrochlorination of Chlordene catalyzed by complexes of water with aluminum and gallium chlorides in DCE are presented in Table 1.

In low-polarity non-donor solvents, water forms strong high-polarity molecular 1 : 2, 1 : 1, and 2 : 1 complexes with aluminum and gallium halides.[15] As follows from the data in Table 1, the 1 : 2 complex possesses catalytic activity, the 1 : 1 and 2 : 1 complexes do not catalyze the hydrochlorination of Chlordene, and the catalysis of the reaction in the presence of the 1 : 1 complex is most likely related to some amount of the 1 : 2 complex present in the solution. According to the published data,[16] the 1 : 2 complex exhibits maximum catalytic activity in the polymerization reaction catalyzed by complexes of water with alkylaluminum chlorides. Thus, ions similar to arenonium ions participate in the hydrochlorination of Chlordene, and the molecular $H_2O \cdot Al_2Cl_6$ complex is the catalyst of this reaction.

Table 1. Hydrochlorination of Chlordene in solutions of complexes of water with aluminum and gallium chlorides in 1,2-dichloroethane

MX_3	C_{MX_3} /mol L^{-1}	C_{H_2O}/C_{MX_3} /mol mol^{-1}	τ_{exp} /min	α_{Ch} (%)
$GaCl_3$	0.0733	0.43	40	98
$GaCl_3$	0.0720	1.09	60	34
$AlCl_3$	0.0963	0.32	15	90
$AlCl_3$	0.0477	0.48	3	99
$AlCl_3$	0.0350	0.53	15	100
$AlCl_3$	0.0383	0.71	15	98
$AlCl_3$	0.0155	1.56	15	0
$AlCl_3$	0.0081	2.84	30	0

Note. Reaction conditions: $T = 293$ K, $V = 30$ cm^3, $w_{HCl} = 0.01$ m^3 h^{-1}, $C_{Chlordene} = 0.391$ mol L^{-1} (where T is temperature, V is the volume of the reaction mass, w is the flow rate of HCl supply, C is the concentration of reagents, τ_{exp} is the time of experiment, and α_{Ch} is the conversion of Chlordene).

Possible complexes $(HCl)_m \cdot (AlCl_3)_n \cdot (H_2O)_k$ (m, n, k = 0—2) were approximated by quantum-chemical calculations to analyze the experimental data obtained, and their reactivity in the gas-phase reactions with different olefins (ethylene, vinylidene chloride, and Chlordene) was evaluated. It can be assumed that in the case of the solvents used with relatively low values of dielectric constant, the contribution of solvation to the enthalpy of the calculated process is low and does not change qualitatively the situation obtained. The PM3 was chosen as the single semiempirical method, which, on the one hand, describes hydrogen bonds, and on the other hand, contains correction parameters for the Al atom.[11]

The data on the total energies of the complex formation calculated as the differences between the total energies of the $(HCl)_m \cdot (H_2O)_k \cdot (AlCl_3)_n$ (m, k, n = 0—2) complexes and their isolated components and the energies of addition of one molecule of H_2O or HCl are presented in Table 2. It can be seen that the total energies of complex formation are maximum in the cases of the $AlCl_3$ dimers. The inclusion of one H_2O molecule in the complex results in destabilization of the system and transforms the complexes into the high-reactive state.

According to the classic concepts on the mechanism of the reaction considered, the energy parameters of the acidity of these complexes, *e.g.*, their energies of deprotonation or dehydroxonation, are the most interesting for estimation of the reactivity.

As follows from the data in Table 3, the deprotonation energy is minimum for the $HCl \cdot AlCl_3$ and $HCl \cdot Al_2Cl_6$ complexes. Since in low-polarity media in the presence

Table 2. Energies of complex formation (ΔE_c, ΔE_{H_2O}, ΔE_{HCl}/eV)

Compound	ΔE_c	ΔE_{H_2O}	ΔE_{HCl}
$H_2O \cdot Al_2Cl_6$	−3.421	−0.513	
$H_2O \cdot AlCl_3$	−1.335	−1.335	
$2H_2O \cdot AlCl_3$	−1.728	−0.393	
$HCl \cdot H_2O$	−0.078	−0.078	−0.078
$HCl \cdot HCl$	−0.163		−0.163
$HCl \cdot HCl \cdot H_2O$	−0.439	−0.275	−0.361
$HCl \cdot Al_2Cl_6$	−3.453		−0.545
$HCl \cdot AlCl_3$	−1.140		−1.140
$HCl \cdot H_2O \cdot Al_2Cl_6$	−3.619	−0.166	−0.198
$HCl \cdot H_2O \cdot AlCl_3$	−2.014	−0.874	−0.679
$HCl \cdot 2H_2O \cdot AlCl_3$	−2.249	−0.235	−0.521
$HCl \cdot HCl \cdot Al_2Cl_6$	−4.656		−1.203
$HCl \cdot HCl \cdot AlCl_3$	−2.056		−0.916
$HCl \cdot HCl \cdot H_2O \cdot Al_2Cl_6$	−4.404	0.252	−0.785
$HCl \cdot HCl \cdot H_2O \cdot AlCl_3$	−2.656	−0.600	−0.642

Note. Energy of formation of a complex calculated per: one H_2O molecule, $\Delta E_{H_2O} = E_{compl.\ with\ H_2O} - E_{compl.\ without\ H_2O} - E_{H_2O}$; one HCl molecule, $\Delta E_{HCl} = E_{compl.\ with\ HCl} - E_{compl.\ without\ HCl} - E_{HCl}$.

Table 3. Deprotonation (ΔE_{H^+}/eV) and dehydroxonation ($\Delta E_{H_3O^+}$/eV) energies

Complex	ΔE_{H^+}	$\Delta E_{H_3O^+}$
$HCl \cdot H_2O$	13.326	7.958
$HCl \cdot HCl$	12.457	
$HCl \cdot HCl \cdot H_2O$	12.263	6.615
$HCl \cdot Al_2Cl_6$	11.678	
$HCl \cdot AlCl_3$	11.430	
$HCl \cdot H_2O \cdot Al_2Cl_6$	11.958	5.726
$HCl \cdot H_2O \cdot AlCl_3$	12.252	6.186
$HCl \cdot 2H_2O \cdot AlCl_3$	12.353	6.369
$HCl \cdot HCl \cdot Al_2Cl_6$	11.713	
$HCl \cdot HCl \cdot AlCl_3$	11.698	
$HCl \cdot HCl \cdot H_2O \cdot Al_2Cl_6$	11.815	5.344
$HCl \cdot HCl \cdot H_2O \cdot AlCl_3$	11.971	6.180

Note. Reactions of deprotonation $Cat \cdot HCl = H^+ + Cl \cdot Cat^-$ and dehydroxonation $HCl \cdot H_2OM_nX_{3n} = H_3O^+ + Cl \cdot M_nX_{3n}^-$.

Table 4. Energies of formation of ion pairs (*E*/eV)

Catalyst	$H_2C{=}CH_2$		$Cl_2C{=}CH_2$		Chlorden	
	H^+	H_3O^+	H^+	H_3O^+	H^+	H_3O^+
H_2O	6.919	6.968	5.826	6.182	6.397	6.650
$HCl \cdot H_2O$	5.856	5.625	4.764	4.838	5.334	5.306
HCl	6.050		4.957		5.528	
Al_2Cl_6	5.271		4.178		4.749	
$HCl \cdot Al_2Cl_6$	5.307		4.214		4.784	
$AlCl_3$	5.023		3.930		4.501	
$HCl \cdot AlCl_3$	5.291		4.198		4.769	
$H_2O \cdot Al_2Cl_6$	5.551	4.736	4.458	3.950	5.029	4.418
$HCl \cdot H_2O \cdot Al_2Cl_6$	5.408	4.354	4.315	3.567	4.886	4.035
$H_2O \cdot AlCl_3$	5.845	5.196	4.752	4.410	5.323	4.878
$HCl \cdot H_2O \cdot AlCl_3$	5.564	5.190	4.471	4.404	5.041	4.872
$2\ H_2O \cdot AlCl_3$	5.947	5.379	4.854	4.593	5.424	5.061

Note. Ion pairs are formed in the reactions: $Olefin + Cat \cdot HCl = Olefin\ H^+ + Cl \cdot Cat^-$, $Olefin + HCl \cdot H_2OM_nX_{3n} = Olefin\ H_3O^+\ Cl \cdot M_nX_{3n}^-$.

of H_2O, the proton most likely exists as H_3O^+, it can be assumed that the proton is transferred in the form of H_3O^+. In fact, calculations show that for the $HCl \cdot HCl \cdot H_2O \cdot Al_2Cl_6$ and $HCl \cdot H_2O \cdot Al_2Cl_6$ complexes, the dehydroxonation energy is ~2 times lower than the deprotonation energy. It noteworthy that the dehydroxonation energy correlates with the catalytic activity of the complexes, because the maximum catalytic activity was observed at the ratio $H_2O : AlCl_3$ = 1 : 2. Note that an increase in the number of H_2O molecules in the complex results in an increase in both the deprotonation and dehydroxonation energies.

The enthalpy of charge transfer (H^+ or H_3O^+) reactions between the complex and olefin is one more important characteristic of the reactivity of the complexes considered in catalytic hydrochlorination of olefins. Ethylene, 1,1-dichloroethylene, and Chlordene were considered as olefins. The calculated data on the energies of formation of the ion pair presented in Table 4 show that the enthalpies of transfer of hydroxonium ions from the $(HCl)_m \cdot H_2O \cdot Al_2Cl_6$ (m = 1, 2) complexes are minimum for all the olefins. It is noteworthy that the data presented were obtained in the "gas-phase" approximation. However, it can be assumed that in the case of nonpolar solvents with relatively low values of dielectric constant, the contribution of solvation to the enthalpy of the processes considered is small and does not change qualitatively the situation obtained.

Thus, $AlCl_3$ participates in the liquid-phase catalytic hydrochlorination of Chlordene in the form of the 1 : 2 complex with water, and water makes easier the transfer of proton (in the form of the hydroxonium ion) from the HCl molecule to olefin.

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