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Conversions of Chlorine-containing Aliphatic Compounds in the Presence of Coordination-unsaturated Metals

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Conversions of aliphatic chlorine-containing compounds (chloroalkenes, chloroalkanes, and derivatives of chloro-substituted carboxylic acids) occur under the action of aprotic acids. Chloroethylenes are polymerised by a cationic mechanism with the formation of oligomeric and polymeric products. The principal reaction of chloroalkanes and chlorocycloalkanes in the presence of salts of coordination-unsaturated metals is dehydrochlorination, which proceeds either intramolecularly or intermolecularly with the formation of polymers with conjugated double bonds. For polychloro-containing compounds, in addition to the dehydrochlorinations, elimination of chlorine occurs. Perchloroalkanes (from C_3 and higher) in the presence of aprotic acids also undergo degradation with breaking of the carbon-carbon bond. There is a bibliography of 353 references.

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I. INTRODUCTION

Chlorine-containing organic compounds are readily available and extremely reactive. They are starting materials for making various organic compounds of practical importance. Many reactions with chlorine-containing products take place in the presence of Friedel–Crafts catalysts. They include the alkylation and acylation of aromatic compounds, addition to alkenes, and replacement of chlorine atoms by other halogens and functional groups and have been discussed in monographs[1-3] and reviews[4-7].

It was noted long ago that reactions involving chlorine-containing compounds in which Lewis acids are used as catalysts are accompanied by conversions of the chlorine-containing reagent itself, which reduces the yield of the main product and contaminates it with various impurities. A characteristic example of such changes is the decarbonylation, in the presence of aluminium chloride, of acyl chlorides with a branch in the α position. Addition of alkyl halides, acyl chlorides, and other compounds to chloroalkenes is accompanied by conversions of each of the reagents separately. In addition to the formation of polyconjugated polymers ("tar"), degradation is observed[4].

Some chloroalkanes and chloroalkenes are widely employed as extractants in heavy organic synthesis (for example, trichloroethylene in the production of ϵ-caprolactam) and in the metallurgical industry for degreasing metal surfaces. Sometimes contact between the solvents used and salts of coordination-unsaturated metals is possible, which brings about the undesirable conversions of the chloroalkanes and chloroalkenes, leading to contamination of the product being extracted and of the solvent.

The reactions of chlorinated hydrocarbons in the presence of Friedel–Crafts catalyst are of independent importance. Thus the dehydrochlorination of chloroalkanes is used for obtaining industrial monomers (vinyl chloride and vinylidene chloride) and trichloroethylene.

The use of chlorine-containing compounds as solvents in the cationic polymerisation of alkenes is well known[8,9]. The part played by the solvent in this is enormous, since the degree of polymerisation of the monomer, the molecular weight, and sometimes also the stereoregularity of the polymer obtained depend partly on it. The effect of the solvent on the course of the polymerisation and the properties of the polymer have recently been linked with the fact that the solvent reacts with the catalyst to form reactive species which participate directly in the polymerisation of the monomer.

Some chlorine-containing compounds can be regarded as models of individual units of such chlorine-containing polymers as poly(vinyl chloride), poly(vinylidene dichloride), chlorinated poly(vinyl chloride), chlorinated polyethylene, etc. Therefore information about the conversions of these compounds in the presence of aprotic acids can be used in studying the mechanism of degradation and analogous conversions of chlorine-containing polymers.

Unlike reactions of organochlorine compounds with other reagents, the conversions of certain solely aliphatic chlorine-containing compounds in the presence of aprotic acids have not been reviewed. The present review is an attempt to survey the available published information on the conversions of chloroalkanes and chloroalkenes in the presence of Lewis acids. This review does not consider the conversions of chlorine-containing aromatic compounds, since the work on this subject has been covered adequately in a monograph[2].

II. CHLOROMETHANES AND THEIR DERIVATIVES

1. CHLOROMETHANES

Chloromethanes are extremely stable compounds and in the absence of atmospheric oxygen they can be stored and distilled without decomposition. The ability of chloromethanes to withstand high temperatures depends on the number of chlorine atoms in them and drops from methyl chloride to chloroform, owing to the decrease in the energy for breaking the C–Cl bond (Table 1). In addition, to high dielectric constants, especially for methyl chloride and methylene dichloride, show that under certain conditions these compounds can be extremely reactive. With such electrophilic compounds as the halides of coordination-unsaturated metals, the chloromethanes form, even at low temperatures (−80, −20°C), stable complexes of the type

$CH_3Cl.AlBr_3$ or $CH_3Cl.Al_2Br_6$, [13,14] in which there is an exchange of halogen atoms between chloromethane and the complex-forming substance [15-17]. With the aid of this reaction, which is effected through a transitional six-membered transition complex [17], carbon tetrabromide can be obtained in high yield from carbon tetrachloride and $AlBr_3$. [18]

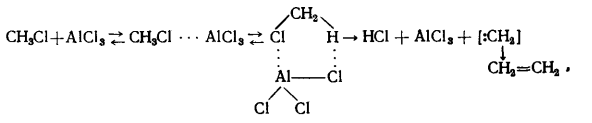
At elevated temperatures more extensive conversions of chloromethanes take place.

Table 1. Characteristics of chloromethanes [10-12].

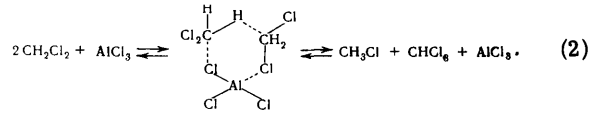
Chloromethane	Decomposition temp., °C	Energy for breaking the C-Cl bond at 400-500°C, kcal mole^{-1}	Energy for breaking the C-H bond at 400-500°C, kcal mole^{-1}	Dielectric constant at 20°C	Distance between chlorine atoms, Å
CH_3Cl	1400	80.5	98.0	12.61	—
CH_2Cl_2	720	73.4	95.0	8.40	3.16
$CHCl_3$	290	66.5	90.2	4.84	3.04
CCl_4	400	76.0	--	2.24	2.58

Methyl chloride. Under the action of $AlCl_3$ at 20°C methyl chloride is converted into hydrogen chloride and ethylene [19]. It could be expected that an intermediate product in the conversion of methyl chloride into ethylene would be ethyl chloride, formed as a result of the condensation of two molecules of methyl chloride. However, the main products of the reaction of ethyl chloride with $AlCl_3$ are polymers [20] (see p. 262) and among the products of the reaction of methyl chloride with $AlCl_3$ neither ethyl chloride nor a polymer were observed. It is also improbable that the conversion of methyl chloride into ethylene proceeds by an ionic mechanism [21,22].

It is assumed [23] that this process is carbenoid in nature and proceeds by intermediate formation of a five-membered transition complex (scheme 1):

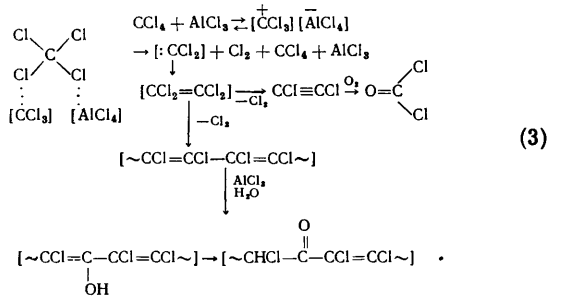

(1)

When a mixture of methylene chloride and $AlCl_3$ is heated to 40°C, a disproportionation (little known for chloroalkanes) takes place, as a result of which methyl chloride and chloroform are formed [19] (scheme 2):

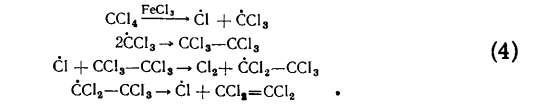

(2)

Furthermore, hydrogen chloride, *trans*-1,2-dichloroethylene, and a polymer of composition $(C_2H_5Cl)_n$ were identified in the reaction products. The formation of 1,2-dichloroethylene from methylene dichloride probably takes place just like the formation of ethylene from methyl chloride, by α-elimination of hydrogen chloride. The polymer $(C_5H_5Cl)_n$ had the same composition and properties as the polymer formed on heating chloroform with the same catalyst to 60°C. Evidently when methylene dichloride is heated with $AlCl_3$, the chloroform which is formed in the disproportionation of methylene dichloride undergoes polycondensation. The polycondensation of chloroform [19] in this instance can be based solely on intermolecular dechlorination. This is shown by the carbon : hydrogen ratio in the polymer, which remains equal to 1 : 1, that is, the same as in the initial chloroform.

In contrast with the other chloromethanes carbon tetrachloride in the presence of $AlCl_3$ undergoes conversions only on heating under severe conditions, for example, at 200°C. [19] Here the main process is the ionisation of the carbon tetrachloride with the formation of the rather stable carbonium ion $\dot{C}Cl_3$. [21,22] The appearance of the carbonium ion is shown by the reaction mass being pink, by absorption in the 530 mμm region, and by the quantitative formation of chloroform in the reaction of carbon tetrachloride with n-hexane in the presence of $AlCl_3$. In addition to ionisation, slight conversion of carbon tetrachloride into dichloroacetylene, carbonyl chloride, and a polymeric product of composition $(C_6H_3Cl_2O_3)_n$ is observed [19]. Dichlorocarbene is evidently an intermediate product of this reaction (scheme 3). The possible formation of dichlorocarbene under similar conditions has already been reported [24]. Support for scheme 3 is provided by the fact that when heated with $AlCl_3$ tetrachloroethylene actually undergoes intramolecular and intermolecular dechlorination with the formation of dichloroacetylene and a polymer (cf. p. 261). The presence of hydrogen and oxygen in this polymer is explained by its interaction with water in the presence of $AlCl_3$: [19]


(3)

The conversions of chloromethanes in the presence of aprotic acids in the gas phase have been little studied. The results published on this subject relate mainly to CCl_4. On passing CCl_4 vapour over iron, zinc, copper, and other metal chlorides at 200–300°C, chlorine, hexachloroethane, and tetrachloroethylene are formed [25-27], that is, the same products as are formed from CCl_4 in high-temperature (700–800°C) pyrolysis [28-32] in the absence of catalysts. According to some results [25-27] the catalytic decomposition of CCl_4 into chlorine, hexachloroethane, and tetrachloroethylene proceeds by a radical mechanism (scheme 4):


(4)

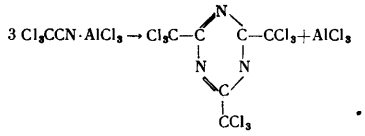
2. SUBSTITUTED CHLOROMETHANES

The replacement of chlorine atoms in chloromethanes by other groups alters the reactivity of the chlorine atoms in chloromethanes. The substituents at which the electronic density is greatest react with aprotonic acids.

Chlorofluoromethanes greatly surpass chloromethanes as regards reactivity in the presence of Lewis acids [33-45]. Under the action of $AlCl_3$ or $AlBr_3$ fluorine-containing chloromethanes readily disproportionate [36-43].

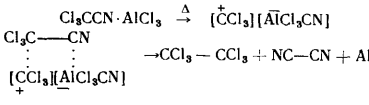
Thus fluoroform is obtained in quantitative yield from dichloro(fluoro)methane at 50°C, [36] whereas under these conditions the disproportionation of chloromethanes is very slow [19].

The introduction of a nitrile group into chloromethanes increases their reactivity even more. The reaction of chloroacetonitriles with aprotic acids begins with complex formation by the nitrile group [2,46,47]. A series of stable complexes of the type $CCl_3CN.MX$, $2CCl_3CN.MX$, and $CCl_2CN.2MX$ is formed. When the complexes are heated to 100°C, trimerisation of the trichloroacetonitrile takes place with the formation of 2,4,6-tris(trichloromethyl)-1,3,5-triazine [46] (scheme 5):



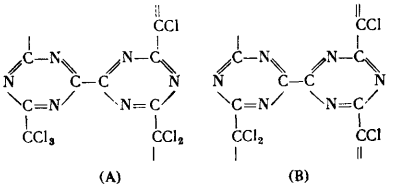
(5)

The same triazine is also obtained by saturation of trichloroacetonitrile with hydrogen chloride in the presence of catalytic amounts of $AlCl_3$ or $AlBr_3$. [48-51] When the complexes of trichloroacetonitrile with $AlCl_3$ are heated to 140–150°C, heterolytic breaking of the carbon–carbon bond of the nitrile occurs, which leads to the formation of hexachloroethane and dicyanogen. The suggested scheme of reaction (6) is confirmed by the formation of chlorotriphenylmethane when the complex $2Cl_3CCN.AlCl_3$ is boiled with benzene. If there were homolytic breaking of the C–C bond the trichloromethyl radical, which is inert in relation to benzene, would be formed [52]:



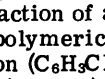
(6)

In addition to hexachloroethane and dicyanogen, when complexes of trichloroacetonitrile with $AlCl_3$ are heated, polymeric products of composition $(C_9Cl_6N_6)_n$ and $(C_9Cl_4N_6)_n$ are formed, which contain units of composition (A) and (B), were obtained:

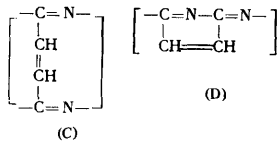


(A) (B)

It has been shown [46] that the formation of these polymers takes place not by the polymerisation of triazine with ring opening [53-55], but by the polymerisation of trichloroacetonitrile and of dicyanogen at the nitrile groups with subsequent dechlorination of the CCl_3 side-groups.

A similar picture is observed in the reaction of dichloroacetonitrile [56] with $AlCl_3$. By heating the complex $2CHCl_2CN.AlCl_3$ to 70°C, 2,4,6-tris(dichloromethyl)triazine can be obtained, which is also formed on prolonged saturation of the nitrile with hydrogen chloride [57]. At temperatures above 80°C the $CHCl_2$ side-groups of the triazine undergo dechlorination under the action of aluminium chloride, with the formation of a polymeric product with conjugated double bonds of composition $(C_6H_3Cl_3N_3)_n$, consisting of triazine rings connected by  bridges [56].

Unlike tri- and di-chloroacetonitriles, monochloroacetonitrile does not trimerise to a triazine in the presence of small quantities of aprotic acids [58]. When the complex $2CH_3ClCN.AlCl_3$ is heated above 200°C, as for other unsaturated nitriles [59-64] polymerisation of the nitrile at the nitrile groups takes place with formation of a chain of conjugated –C=N– bonds. Simultaneously with the polymerisation, dehydrochlorination of the chloromethyl side-groups takes place, as a result of which units of types (C) and (D) arise in the polymer.



(C) (D)

Chloroacetyl chlorides can be regarded as chloromethanes in which the central carbon atom is connected, not solely with chlorine and hydrogen atoms, but also with the  group. As for other acyl chlorides [65,66], the reaction of these compounds with salts probably begins with the formation of complexes of type .$AlCl_3$ or .Al_2Cl_6, in which exchange of halogen atoms between the acyl chloride and the salt can take place [67]. There are differences of opinion concerning the reaction centre in acid chlorides in the formation of complexes. Some consider [6,68-70] that the active centre in organic acyl chlorides is the oxygen of the carbonyl group and with aprotic acids complexes of the following type are formed:



However, it has been shown [71] by infrared spectroscopy that the chlorine in the acyl chloride is subjected to electrophilic attack by the aluminium chloride, which leads to the formation of an ion-pair $[R\overset{+}{C}{=}O][\overline{Al}Cl_4]$. Such a viewpoint is maintained by Palmer and McVie [72]. It has recently been shown [73] spectroscopically that both types of complex formation occur and the predominance of one over the other depends primarily on the structure of the initial acyl chloride. Electron-donating substituents in the acid residue of the acyl chloride increase the electron density in the –COCl group, which facilitates reaction with aprotic acids at the oxygen atom. Electron-withdrawing substituents depress the nucleophilic properties of the oxygen atom and therefore the complex with the catalyst is formed preferentially at the chlorine atom. This evidently relates to a compound such as trichloroacetyl chloride.

When the complexes of acyl chlorides and aprotic acids are heated, they decompose with the liberation of carbon monoxide and the formation, usually, of the corresponding alkyl chlorides [74-81]. Electron-donating substituents in the acid residue accelerate the elimination of carbon monoxide, and electron-withdrawing substituents retard it [82-84]. In this connection the decarbonylation of the acid chlorides in the last instance is carried out at high temperatures and in the presence of large amounts of catalyst. According to these results, when trichloroacetyl chloride is heated to 100°C in the presence of aluminium chloride decomposition of the acid chloride by scheme (7) to carbon

monoxide and carbon tetrachloride takes place[85,86]. In addition to the compounds mentioned, conversion products of CCl_4 (see scheme 3) are also formed—dichloroacetylene and a polymer[86]:

$$CCl_3C(=O)\cdots AlCl_3 \xrightarrow{\Delta} [CCl_3C{\equiv}O^+][\overline{A}lCl_4] \rightarrow CO + [\overset{+}{C}Cl_3][\overline{A}lCl_4] \quad (7)$$

$$[\overset{+}{C}Cl_3][AlCl_4] \rightarrow CCl_4 + AlCl_3 \quad .$$

When dichloroacetyl chloride is heated with aluminium chloride in chloroform solution it also decomposes with release of carbon monoxide[87]. When a mixture of chloroacetyl chloride and aluminium chloride is heated there is an intensive evolution of carbon monoxide and also of hydrogen chloride and chloroacetylene and the formation of a polymeric product with conjugated double bonds and a carbon : hydrogen : chlorine ratio of 4 : 4 : 1.[86] The decomposition of chloroacetyl chloride probably takes place just like the decomposition of trichloroacetyl chloride (scheme 7), that is, through the intermediate production of an acylcation, reaction of which is effected by loss of carbon monoxide[88]. Here the formation of hydrogen chloride and chloroacetylene is due to secondary conversions of methylene dichloride.

Carbonyl chloride with aprotic acids gives stable complexes[69,89] in which exchange of halogen atoms takes place[67]. In the gas phase at 300–400°C[90,91] under the action of aprotic acids decomposition of carbonyl chloride takes place with the formation of carbon monoxide and carbon tetrachloride.

In esters of chloroacetic acids, as in the acyl chlorides of these acids, reaction with Friedel–Crafts catalyst occurs first at the ester group. At low (−20°; +30°C) temperatures, esters of trichloroacetic acid and $TiCl_4$ form unstable complexes of composition $2TiCl_4.CCl_3COOR$, $TiCl_4.CCl_3COOR$, and $TiCl_4.2CCl_3.COOR$.[92,93] The lower stability of these complexes in comparison with esters of unsubstituted aliphatic acids[94–100] is due to the increased electron-withdrawing properties of the CCl_3 group. Spectroscopic investigations in recent years have shown convincingly that complex formation by esters with the salts of coordination-unsaturated metals is effected at the carbonyl oxygen of the ester group[101–106].

Careful heating of the complexes of esters with aprotic acids caused them to melt and dissociate into the initial components. Above the melting points of the complexes and also in the presence of large quantities of aprotic acids some esters decompose readily with formation of alkyl halides and salts of organic acids[107–110]. An analogous picture is also observed on heating a mixture of methyl trichloroacetate and aluminium chloride, taken in a ratio between 1 : 1 and 3 : 1. Methyl chloride and bis(trichloroacetate)–aluminium chloride were thus obtained[111]. When the reaction was carried out under more severe conditions (higher temperature, increase in the excess of $AlCl_3$) tetrachloroethylene appeared in the reaction products in addition to the compounds listed above[111]. The formation of these compounds can be explained with the aid of schemes (8) and (9), according to which complexes (A) and (B) arise as intermediate products of the reaction; in the latter there is exchange of a chlorine atom of aluminium chloride for the acid residue of the ester:

$$\underset{(A)}{CCl_3{-}C(=O\cdots AlCl_3){-}OCH_3} \rightleftarrows \underset{(B)}{CCl_3{-}C(=O\rightarrow AlCl_3){-}OCH_3} \quad , \quad (8)$$

$$CCl_3C(=O\rightarrow Al(Cl)Cl){-}O{-}CH_3 \xrightarrow{\Delta} CCl_3C(=O){-}OAlCl_2 + CH_3Cl \xrightarrow{\Delta}$$

$$[CCl_3^-] \xrightarrow{-Cl^-} [:CCl_2] \rightarrow CCl_2{=}CCl_2 \quad . \quad (9)$$

The aluminium salt of trichloroacetic acid, like the other salts of this acid[112,113], is further decarboxylated with the formation of the carbanion CCl_3^-, which is converted into dichlorocarbene and then into tetrachloroethylene. The intermediate formation of the $\overline{C}Cl_3$ anion is shown by the fact that when the reaction mass is treated with water chloroform is observed in the products[111].

In the presence of salts of coordination-unsaturated metals alkyl chloroformates readily decompose with liberation of carbon dioxide and an alkyl halide[114,115].

The formation of aluminium salts and chloroalkanes in the reaction of esters with $AlCl_3$ enables the effect of the structure of the esters on their ability to acylate and alkylate aromatic compounds after Friedel–Crafts to be explained. Esters of aliphatic alcohols and organic acids which contain electron-withdrawing substituents (chloroacetic, trichloroacetic, $\alpha\beta$-dichloropropionic, benzoic, oxalic, etc.) only alkylate benzene, since the aluminium salts of these acids exhibit weak acylating properties[111]. Conversely, esters of aliphatic alcohols and unsubstituted aliphatic acids give with benzene both alkylation products and acylation products, since the aluminium salts then formed exhibit high acylating properties[108,110,111,116,117]. And, finally, esters containing electron-withdrawing substituents simultaneously in both the acid and the alcohol radicals do not enter into any reaction with benzene in the presence of Friedel–Crafts catalysts. In this instance the ester probably does not decompose into salt and alkyl halide.

Phenyl-substituted chloromethanes are distinguished by high reactivity. The presence of phenyl groups creates increased electron density at the chlorine atom, as a result of which its mobility increases sharply. The polycondensation of benzyl chloride in the presence of aprotic acids is undoubtedly of interest[118–132]. This reaction was described in detail in a recently published review[133] and allows thermally stable polymers to be obtained from saturated chlorine-containing compounds.

The chlorine in chlorotriphenylmethane is even more labile than that in benzyl chloride. Under the action of Friedel–Crafts catalysts chlorotriphenylmethane dissociates readily with the formation of a stable carbonium ion[134–136]. Here the degree of ionisation of chlorotriphenylmethane depends considerably on the nature of the catalyst and the solvent. In their ability to eliminate a chlorine ion from chlorotriphenylmethane the catalysts are arranged in the following series: $SbCl_5 \simeq FeCl_3 > GaCl_3 > SnCl_4 > BCl_3 > ZnCl_2 > TiCl_4 > SbCl_3 > AlCl_3 > PCl_5$.

III. CHLOROALKENES

1. CHLOROETHYLENES

Chloroethylenes which contain one or two chlorine atoms (vinyl chloride, vinylidene dichloride, and 1,2-dichloroethylene) are stable at high temperatures in the absence of atmospheric oxygen[137–141]. Vinyl chloride does not lose hydrogen chloride even when treated with bases[139].

The extremely high stability of these chloroethylenes, owing to the low mobility of their chlorine atoms, is used for the preparation of vinyl chloride, vinylidene chloride, and 1,2-dichloroethylene by pyrolysis of the corresponding chloroethanes[137,140]. The low lability of the chlorine atoms in these chloroethylenes is explained by the presence of conjugation between the unshared electron pairs of the chlorine atoms and the double bond:

$$CH_2{=}CCl_2 \leftarrow \overset{+}{C}H_2{-}CCl{=}\overset{+}{C}l.$$

Owing to this, the distance between the carbon and chlorine is shortened and becomes less (Table 2) than in saturated chlorinated hydrocarbons (for example, it is 1.77 Å in ethyl chloride).

Trichloroethylene and tetrachloroethylene, unlike the mono- and di-chloroethylenes, are unstable during storage and when heated. To suppress dehydrochlorination and other side-reactions, tri- and per-chloroethylenes were distilled in the presence of stabilisers[142-146]—hydrazones[144,145], epoxy-compounds[146], etc. The diminished thermal stability of trichloroethylene and tetrachloroethylene is due to the greater lability of the chlorine atoms in them. This is shown by the lower ionisation potentials and the increase in the C–Cl bond length in these compounds (Table 2).

Table 2. Characteristics of chloroethylenes[10,147,148].

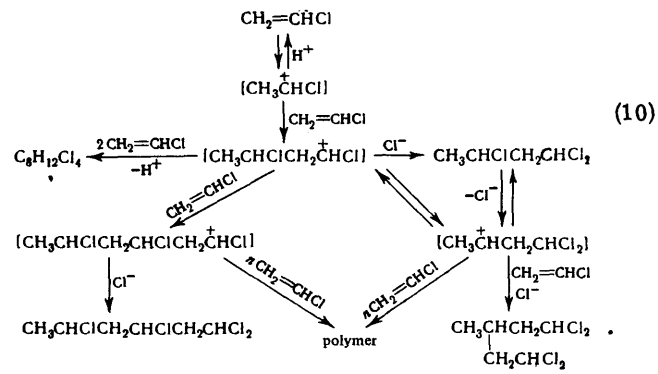
Chloroethylene	Ionisation potential, eV	C–Cl distance, Å	Dipole moment in benzene, D
$CH_2{=}CHCl$	9.99	1.69	1.44
$CH_2{=}CCl_2$	9.79	1.69	1.40
cis-CHCl-CHCl	9.66	1.67	1.85
trans-CHCl=CHCl	9.96	1.69	0.0
$CHCl{=}CCl_2$	8.80	1.82	0.94
$CCl_2{=}CCl_2$	9.50	1.82	0.0

The behaviour of chloroethylenes in the presence of aprotic acids is also different.

From the nature of the changes which chloroethylenes undergo in the presence of Lewis acids they can be divided into two groups. The first group of chloroethylenes (vinyl chloride, vinylidene chloride, and both isomers of 1,2-dichloroethylene) has a tendency to polymerise by a cationic mechanism in the presence of aprotic acids[138,139,149-156]. Trichloroethylene and tetrachloroethylene constitute a second group and are distinguished from the representatives of the first group by their undergoing autocondensation under the action of cationic catalysts.

a. Polymerisation of Chloroethylenes

Vinyl chloride is readily protonated in the presence of cationic catalysts ($AlCl_3$ or $TiCl_4$) owing to the moistness of the catalyst, with the formation of the reactive carbonium ion $CH_3\overset{+}{C}HCl$. This positively charged species, like other carbonium ions[159,160] initiates further polymerisation of vinyl chloride at –10°C[154-156] with the formation of oligomeric and polymeric products (scheme 10). The reaction of the $CH_3\overset{+}{C}HCl$ cation with a molecule of vinyl chloride leads to the formation of a new carbocation $CH_3CHClCH_2\overset{+}{C}HCl$, which is partly neutralised by the chlorine anion with the formation of trichlorobutane[154-158]. Furthermore, by successive addition of one or two molecules of vinyl chloride the dimeric cation is converted further into 1,1,3,5-tetrachlorohexane and tetrachloro-octene. Simultaneously, the cation $CH_3CHClCH_2\overset{+}{C}HCl$ isomerises into the cation $CH_3\overset{+}{C}HCH_2CHCl_2$. The latter reacts with vinyl chloride and is converted into 1,1,5,5-tetrachloro-3-methylpentane. As a result of further chain growth and secondary conversions of the oligomeric compounds with the vinyl chloride a low-molecular-weight polymer with a degree of polymerisation of ~ 30 is obtained, which consists of (–CH=CH–) and ($-\underset{\displaystyle CH_2CHCl_2}{\underset{|}{CH}}-CH_2-$) units in the ratio 1 : 1[154-156].



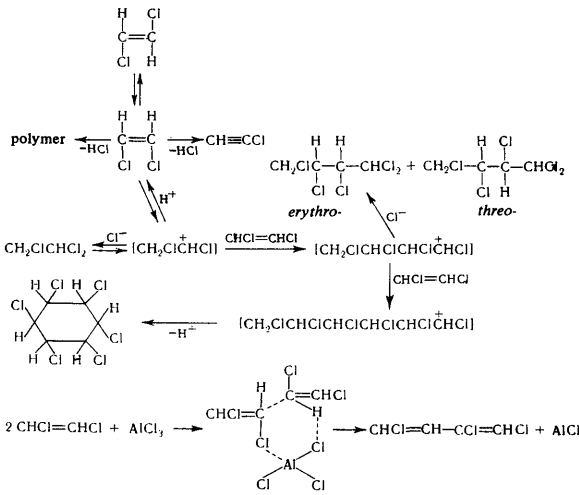
Raising the polymerisation temperature of vinyl chloride to 0°C or over accelerates the reaction, but simultaneously increases the rate of dehydrochlorination of the polymeric product formed. Therefore the polymer contains up to 80% vinylene units[154-156].

Owing to its asymmetric structure and comparatively large dipole moment (Table 2), *cis*-1,2-dichloroethylene is more reactive than the *trans*-isomer[147,161,162]. This is also true of reactions in the presence of aprotic acids. At room temperature under the influence of $AlCl_3$ both isomers of 1,2-dichloroethylene undergo only mutual interconversions into one another (scheme 11)[152]. The isomerisation of *trans*-1,2-dichloroethylene is effected at a greater rate than that of the *cis*-isomer[163,164].

The cationic polymerisation of 1,2-dichloroethylene is effected only at 50–70°C and is broken at the stage of formation of a dimeric compound (mixture of *erythro*- and *threo*-isomers of 1,1,2,3,4-pentachlorobutane)[152,155,156,165] and the trimer α-1,2,3,4,5,6-hexachlorocyclohexane[152,156]. Further polymerisation of 1,2-dichloroethylene does not take place, since the dimers give stable and unreactive complexes with the catalyst ($AlCl_3$) and the trimeric cation is cyclised (scheme 11). Furthermore, under these conditions under the influence of aluminium chloride pseudo-ionic processes of intramolecular and intermolecular dehydrochlorination of 1,2-dichloroethylene and its polymerisation products occur, as a result of which chloroacetylene and a polymeric product consisting of (–CH=CCl–) and ($\rangle C{=}CHCl$) units are formed[152].

Intermolecular dehydrochlorination of 1,2-dichloroethylene can be effected in the transition complex by

simultaneous electron transfer (scheme 12). The hydrogen chloride thereby liberated reacts with 1,2-dichloroethylene, which leads to the formation of 1,1,2-trichloroethane [152,166].

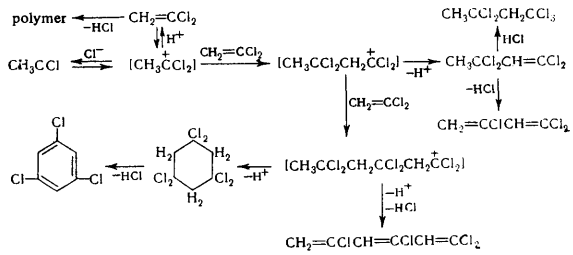


(11)

(12)

Vinylidene chloride at −50°C in the presence of $AlCl_3$ gives low-molecular-weight products of the polymerisation: the dimer [167] 1,1,3,3-tetrachlorobutene [150] and a cyclic trimer, 1,1,3,3,5,5-hexachlorocyclohexane [150]. On raising the temperature the polymerisation is accompanied by disproportionation of the 1,1,3,3-tetrachlorobutene to 1,1,1,3,3-tetrachlorobutene to 1,1,1,3,3-pentachlorobutane and 1,1,3-trichlorobutadiene (scheme 13), and also by dehydrochlorinations, as a result of which unsaturated compounds are formed: 1,1,3,5-tetrachlorohexatriene, 1,3,5-trichlorobenzene and a polymer with conjugated double bonds and with a composition close to $(CH_2Cl)_n$.

In the presence of $ZnCl_2$, which is a weaker complex-forming substance and cyclising agent than $AlCl_3$, vinylidene chloride is smoothly polymerised at 30°C with the production of poly(vinylidene chloride) [153]. This polymer is distinguished from the poly(vinylidene chloride obtained by radical polymerisation [168] by higher crystallinity [153].



(13)

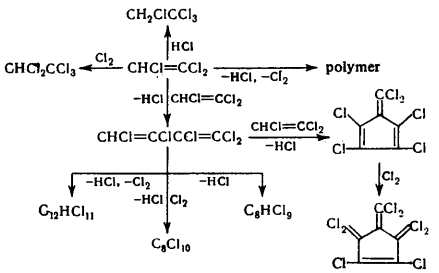
Hence the structure of chloroethylenes and the stability of the carbonium ions formed from them are the deciding factors in cationic polymerisation of these monomers. The chloroethylenes can be arranged according to their ability to polymerise in the following order [156]:

$$CH_2=CCl_2 > CH_2=CHCl > CHCl=CHCl\ [156].$$

It is noteworthy that in the case of vinyl chloride polymerisation in the presence of $AlCl_3$ leads to polymeric products, whereas with vinylidene chloride and 1,2-dichloroethylene the polymerisation is broken at the stage of cyclic trimer formation. Cyclisation of the trimeric cations is explained by the curvature of these cations in space and the possibility of a release of energy in the formation from them of uncharged six-membered rings [169].

b. Autocondensation of Chloroethylenes

For trichloroethylene the tendency to autocondensation is even greater than for 1,2-dichloroethylene (p. 260). In the presence of $AlCl_3$ trichloroethylene loses HCl even at −10°C. [170] As for 1,2-dichloroethylene, the autocondensation of trichloroethylene is probably effected by a pseudo-ionic mechanism and leads to the formation of oligomeric and polymeric products (scheme 14) [170,171]. Here the dimeric product [166,170-176] is a mixture of the *cis*- and *trans*-isomers of 1,1,2,3,4-pentachlorobutadiene [170,171].



(14)

The polycondensation of trichloroethylene and of the products of the oligomerisation to a polymeric product containing units of the −CCl=CCl− type and five-membered rings, proceeds both by dehydrochlorination and by dechlorination. The hydrogen chloride and chlorine thus liberated are partly consumed in the reaction with unsaturated compounds, which leads to the appearance among the reaction products of non-symmetric tetrachloroethane [170] and pentachloroethane [171].

On heating a mixture of tetrachloroethylene and aluminium chloride to 100–110°C, intermolecular and intramolecular dechlorination of tetrachloroethylene occur, with the formation of dichloroacetylene, hexachloroethane, and a polymeric product with conjugated double bonds [19], analogous in composition and properties to the polymer obtained from CCl_4 (cf. scheme 3).

Hence, autocondensation of chloroethylenes under the action of $AlCl_3$ takes place readily in those instances when the chlorine atoms in chloroethylenes (trichloroethylene and tetrachloroethylene) exhibit sufficient lability (cf. Table 2).

2. OTHER CHLOROALKENES

Chloroalkenes without chlorine atoms or with one or two chlorine atoms polymerise according to a cationic mechanism with the formation of oligomeric [177-180] and polymeric [181-183] products. Thus in the presence of $AlCl_3$ at 50°C allyl chloride gives di-, tri-, tetra-, and pentamers [180] which have the structure

$$CH_3CH-[CH_2CH-]_nCH=CHCH_2Cl.$$
$$\quad\ CH_2Cl \qquad\ CH_2Cl$$

On raising the temperature to 100–200°C the depth of the polymerisation of the allyl chloride is greatly increased [182,183]. However, simultaneously with this, dehydrochlorination of the polymerisation products takes

place, which leads to the production of a polymer containing unsaturated links of the type $-CH_2-\overset{}{\underset{}{C}}=CH_2$ type in addition to allyl chloride units[183].

The polymerisation[181] of methyl-substituted allyl chloride—3-chloro-3-methylbut-1-ene—in the presence of $AlCl_3$ is accompanied by exchange of the chlorine atom and methyl group, which leads to the production of a polymer containing different units[181,184-186].

Polychlorine-containing alkenes with aprotic acids form stable, often coloured, complexes[4,187] in which exchange of halogen atoms between the chloroalkene and catalyst takes place[188-191]. The exchange by the halogens is used for obtaining chlorofluoroalkenes; exchange proceeds readily on heating chloroalkenes with fluorides of coordination-unsaturated metals[188-190] (for example, scheme 15).

$$CCl_2=CClCHCl_2 \xrightarrow{SbF_5} CCl_2=CClCHF_2 \qquad (15)$$

The process of halogen exchange is usually accompanied by rearrangements[190] and disproportionation[192]. Here there is a tendency to accumulate fluorine atoms at one carbon atom of the chloroalkene.

At high temperatures (100–200°C) complexes of polychloroalkenes with aprotic acids undergo deeper changes; in addition to the halogen exchange dehalogenation and heterolytic breaking of the carbon–carbon bond take place[40,193]. Thus on heating a mixture of hexachloropropene with $AlCl_3$ to 160°C, CCl_4, hexachlorobutadiene, tetrachloroethylene and conversion products of tetrachloroethylene (dichloroacetylene, hexachloroethane, and a polymeric product with conjugated double bonds) are formed[193] (scheme 16).

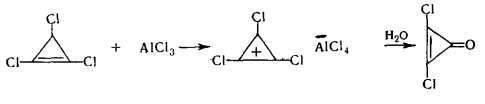
$$CCl_2=CClCCl_3\cdot AlCl_3 \rightleftarrows [CCl_2=CClCCl_3][\overline{A}lCl_4] \rightleftarrows [CCl_2=\overset{+}{C}Cl]\,[\overline{A}lCl_3CCl_3]$$
$$[\overline{A}lCl_3CCl_3] \rightarrow [:CCl_2] + AlCl_4^- \rightarrow CCl_2=CCl_2 + AlCl_4^-$$
$$CCl_4 + AlCl_3 \qquad (16)$$
$$\uparrow$$
$$[CCl_2=CCl]^+ + [AlCl_4] \xrightarrow{CCl_2=CClCCl_3} CCl_2=CClCCl=CCl_2 + [\overset{+}{C}Cl_3][\overline{A}lCl_4]$$

In addition to the breaking of the carbon–carbon bond, autocondensation of polychloroalkenes takes place with release of hydrogen chloride and chlorine[187,194] and the production of dimeric compounds. Perchloroalkenes which contain five or more carbon atoms in a chain are readily cyclised under the action of $AlCl_3$ into five- and six-membered rings[4,30], for example, by scheme (17). Here the cyclisation of the perchloroalkenes sometimes takes place with isomerisation of the carbon skeleton[194] and breaking of the carbon–carbon bond.

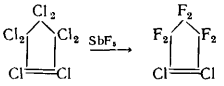
$$CCl_2=CClCCl=CClCCl_3 \xrightarrow{-Cl_2} Cl_2\langle\overset{Cl}{\underset{Cl}{=}}\rangle\overset{Cl}{\underset{Cl}{=}} \qquad (17)$$

Thus, heating decachloromethylpentadiene in the presence of $AlCl_3$ leads to the production of CCl_4 and hexachlorocyclopentadiene[195].

The conversions of perchlorinated cycloalkenes, which form extremely stable complexes with aprotic acids, are interesting. The complex of tetrachlorocyclopropene with $AlCl_3$ has the properties of an organic salt, since the trichlorocyclopropylium cation which is formed is very stable[196-201]. On treatment with water, this salt is hydrolysed with release of dichloropropenone according to scheme (18).


(18)

Heating the complexes of perchlorinated cycloalkenes with aprotic acids leads to vigorous exchange of halogens between the cycloalkene and catalyst[199-200] (scheme 19). The allyl chlorine atoms are exchanged first[189]:


(19)

Heating such complexes sometimes leads to the isomerisation of a cycloalkene[203] and to the formation of dimeric products[202]. Dimerisation proceeds with opening of the double bonds[195].

IV. CHLOROALKANES

1. CHLOROETHANES

Chloroethanes are comparatively unstable compounds. Some of them decompose with release of HCl even during storage and distillation. The hydrogen chloride of nonsymmetric chloroethanes is lost most easily[204-206]. To increase the thermal stability of chloroethanes stabilisers are added to them[204-207], for example, aliphatic hydroxyacids[207] and epoxy-compounds[205].

Aprotic acids accelerate the dehydrochlorination of chloroethanes, which, like halogen exchange[212-214], is effected through the intermediate formation of complexes of the $CH_3CH_2Cl.Al_2Cl_6$ type[208-211]. Loss of HCl takes place at temperatures considerably lower than the boiling points of the chloroethanes[215,216]. For chloroethanes with a $CHCl_2$ group the thermal stability in the presence of aluminium chloride increases with the degree of chlorination of the neighbouring methyl group, that is,

$$CH_3CHCl_2 < CH_2ClCHCl_2 < CHCl_2CHCl_2,$$

but drops again on going to pentachloroethane[216]. The rate of dehydrochlorination of chloroethanes with a CH_3 group under the action of the same reagent increases with the content of chlorine atoms in the neighbouring methyl group[216]:

$$CH_3CH_2Cl < CH_3CHCl_2 < CH_3CCl_3 .$$

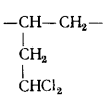
The structure of the initial chloroethanes shows the effect not only on the rate of dehydrochlorination in the presence of aprotic acids but also on the composition of the conversion products of the chloroethanes.

In the presence of $AlCl_3$ at 35–40°C ethyl chloride undergoes a mainly intermolecular dehydrochlorination with the formation of polymeric products with a molecular weight of up to 700 and containing ethylidene units $-\underset{CH_3}{\overset{|}{C}}H-$ and carbonyl groups in a ratio of between 10:1 and 30:1.[20] The appearance of carbonyl groups in the polymer is explained[217] by its oxidation at the double bonds. In the reaction of ethyl chloride with $AlCl_3$, in addition to the polymer a little ethylene is also formed, owing to intramolecular $\alpha\beta$-*cis*-elimination of hydrogen chloride from the ethyl chloride. The predominance of intermolecular dehydrochlorination over intramolecular is because there is a high probability of collision of the $CH_3CH_2Cl.AlCl_3$ complexes with one another in the liquid phase. Because the hydrogen in the CH_2Cl group of ethyl chloride is more labile than that in the $-CH_3$ group, intermolecular dehydrochlorination proceeds mainly with involvement of the chloromethyl group. In the dehydrochlorination of ethyl

chloride on metal chlorides ($NiCl_2$, $FeCl_3$, $AlCl_3$) in the vapour phase (300°C) the probability of collision of two molecules of ethyl chloride on the surface of the catalyst is low. Therefore under these conditions there is mainly intramolecular loss of hydrogen chloride with the formation of ethylene[4] and a polymeric product is only produced in small quantities.

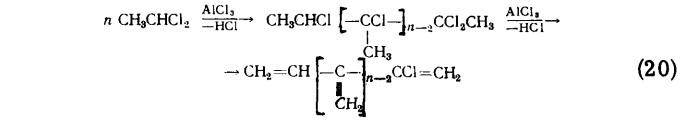
Dichloroethanes. At room temperature and in the presence of small quantities of aluminium chloride there is slight isomerisation of 1,2-dichloroethane into 1,1-dichloroethane[218,219]. This compound is considerably more reactive than its symmetric isomer. Under the action of $AlCl_3$ 1,1-dichloroethane undergoes intramolecular loss of hydrogen chloride with the formation of small quantities of vinyl chloride even at 0°C.[215,219] Furthermore, at 30°C it partly rearranges into the symmetric isomer[219]. At 50–60°C both isomers of dichloroethane undergo intermolecular dehydrochlorination with the quantitative formation of polymeric products with conjugated double bonds[220,221]. The polymeric products of composition $(C_2H_2)_n$ contain predominantly vinylene –CH=CH– (I) and vinylidene $\diagdown C{=}CH_2$ (II) units[221]; they are not polyphenylethylenes, as was suggested earlier[222].

Polymeric products with I and II links cannot be obtained in the dehydrochlorination of poly(vinyl chloride), which is in turn formed by polymerisation of vinyl chloride as already proposed[353]. The present authors heated a mixture of vinyl chloride and $AlCl_3$ under conditions for the polycondensation of dichloroethanes and obtained the same products as were described above (cf. scheme 10). The polymer thus obtained contained mainly the link



and did not contain I units.

Since the reactivities of both the CH_2Cl groups in 1,2-dichloroethane are the same, and in 1,1-dichloroethane the more reactive group is $CHCl_2$,[221] the vinylidene units are formed from 1,1-dichloroethane (scheme 20):



(20)

Mouneyrat[223] obtained tetrabromoethane by heating 1,2-dibromoethane in the presence of bromine and aluminium bromide. From this he concluded that dihalogenoethanes undergo intramolecular dehydrohalogenation on Friedel–Crafts catalysts to acetylene, which then adds bromine and is converted into tetrabromoethane. Evidently, Mouneyrat was wrong, since under the conditions of his experiments the usual bromination, catalysed by aprotic acid[1], should take place. We heated 1,2-dibromoethane in the presence of aluminium bromide or chloride and obtained a polymeric product which is analogous in composition and properties to the polymer obtained from 1,2-dichloroethane.

It is noteworthy that the polymers based on dichloroethanes are, like other poly-conjugated systems[224], thermostabilisers of chlorine-containing compounds[216].

The vapour-phase intramolecular dehydrochlorination of the two dichloroethanes is of interest as an industrial method of obtaining vinyl chloride[225]. The reaction is effected at 300–400°C on acid catalysts (chlorides of zinc, magnesium, iron, aluminosilicate, etc.)[225–228]. Here small quantities of resinous substances are formed as well as vinyl chloride. Furthermore, under these conditions there is also isomerisation of the symmetric isomer of dichloroethane into the non-symmetric[218]. The almost selective dehydrochlorination of dichloroethanes in the vapour phase to vinyl chloride is because here there is little probability of collision of even two molecules of dichloroethane on the catalyst surface. The use of inert gases as diluents has been proposed[229] to even further reduce the probability of such collisions and decrease the formation of resinous substances[229].

1,1,2-Trichloroethane undergoes intramolecular and intermolecular dehydrochlorination in the liquid phase in the presence of $AlCl_3$.[152] Intramolecular elimination of hydrogen chloride to give 1,2-dichloroethylene (mainly the *trans*-isomer)[215] is effected through the intermediate formation of the carbonium ion $CH_2Cl–\overset{+}{C}HCl$. The 1,2-dichloroethylene which is formed reacts further by a cationic mechanism according to scheme (11). The chief reaction which takes place in the reaction of 1,1,2-trichloroethane with $AlCl_3$ is polycondensation with the formation of a polymeric product with conjugated double bonds, including the units –CH=CCl– and $-C(=CHCl)-$ in the ratio 1:1.[152]

In the vapour phase on acid catalysts 1,1,2-trichloroethane undergoes $\alpha\beta$-elimination of hydrogen chloride with predominant formation of *cis*-1,2-dichloroethylene[228,230,231]. Vinylidene dichloride is obtained in addition to 1,2-dichloroethylene[228,230].

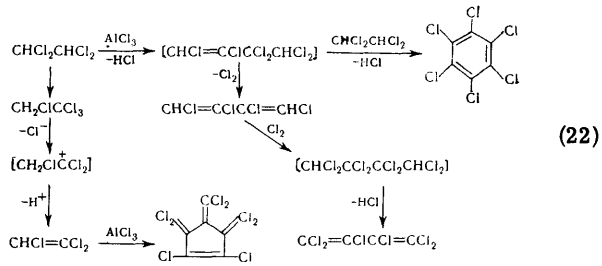
1,1,1-Trichloroethane can be quantitatively converted into vinylidene chloride in the liquid phase under the action of $FeCl_3$.[184,231] In the presence of $AlCl_3$, 1,1,1-trichloroethane also loses hydrogen chloride intramolecularly[150]. However, the vinylidene chloride thus formed is converted further into 1,1,3,3-tetrachlorobutene and 1,1,3,3,5,5-hexachlorocyclohexane under the influence of $AlCl_3$ (cf. scheme 13). The preferential intramolecular dehydrochlorination of 1,1,1-trichloroethane is explained by the fact that this compound, unlike 1,1,2-trichloroethane, gives the relatively stable carbonium ion $CH_3\overset{+}{C}Cl_2$ on reaction with $AlCl_3$. The ionic mechanism of dehydrochlorination of 1,1,1-trichloroethane on acid catalysts[228] is also retained on carrying out the reaction in the vapour phase.

Non-symmetric tetrachloroethane behaves similarly to 1,1,1-trichloroethane in the presence of aprotic acids; in the liquid phase it is smoothly dehydrochlorinated to trichloroethylene[184,215,219,231,232]. Here in addition to trichloroethylene the products are 1,2,3,4,4-pentachlorobutadiene, perchlorofulvene, and 1,2,3,3,5,5-hexachloro-4-(dichloromethylene)cyclopentene[219], which are conversion products of trichloroethylene (see scheme 14).

Non-symmetric tetrachloroethane is smoothly converted into trichloroethylene in the vapour phase on metal chlorides[233,234].

When 1,1,2,2-tetrachloroethane is heated with $AlCl_3$ in the liquid phase, intermolecular dehydrochlorination occurs with the formation of dimeric compounds—1,2,3,4-tetrachlorobutadiene and hexachlorobutadiene—the trimer hexachlorobenzene, and the polymer of composition $(C_6HCl_4)_n$ (scheme 22)[235]. Here the intermolecular elimination of HCl from tetrachloroethane is accompanied by

dechlorination and chlorination, owing to the presence of tetrachlorobutadiene and hexachlorobutadiene among the reaction products. A polymeric product is also the result not only of dehydrochlorination but also the loss of chlorine, and contains five- and six-membered rings.

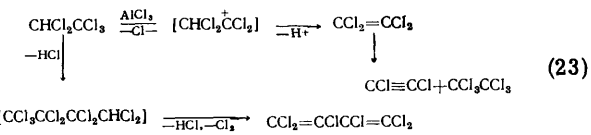


(22)

When 1,1,2,2-tetrachloroethane is heated with $AlCl_3$ in addition to polycondensation it undergoes isomerisation into the non-symmetric isomer[235,236], which under the conditions of the reaction loses HCl intramolecularly with the formation of trichloroethylene.

Dehydrochlorination of symmetric tetrachloroethane on acid catalysts in the vapour phase leads to a mixture of products in which trichloroethylene predominates[228]. In addition to trichloroethylene, tetrachloroethylene, pentachloroethane, and hexachloroethane are also observed[237]. Probably, dehydrochlorination of tetrachloroethane in the vapour phase takes place by a radical mechanism.

Pentachloroethane, like other chloroethanes with the CCl_3 group, forms the stable carbonium ion $CHCl_2-\overset{+}{C}Cl_2$ in the presence of aprotic acids, and this ion is further converted into tetrachloroethylene[215,219,238,239]. In the presence of large quantities of $AlCl_3$ (pentachloroethane : $AlCl_3$ ratio 5 : 1) in the liquid phase (120–150°C) dichloroacetylene, hexachloroethane, and hexachlorobutadiene are formed in addition to tetrachloroethylene[219]. The conversion of pentachloroethane under these conditions take place by scheme (23).



(23)

Tetrachloroethylene is the only product of the pyrolysis of pentachloroethane in the vapour phase (200–350°C) in the presence of aprotic acids[30,240].

Hexachloroethane is very stable on heating, as [might be expected of] a symmetrically constructed compound[30]. In the presence of aprotic acids at 200–250°C (in an ampoule) it does not undergo any changes in the liquid phase[19]. In the vapour phase at 300–400°C on Lewis acids, hexachloroethane is destroyed by a radical mechanism with the formation of tetrachloroethylene and chlorine[25–27].

2. SUBSTITUTED CHLOROETHANES

Replacement of the chlorine atoms in chloroethanes by more electronegative groups (*p*-chlorophenyl[241], fluorine[242]) retards the dehydrochlorination of chloroethanes. In addition there is an increase in the tendency of chlorofluoroethanes to undergo rearrangements[42,242–245]. Isomerisation of chlorofluoroethanes in the presence of aprotic acids proceeds in such a manner that the fluorine atoms are grouped on one carbon atom with the formation of the CF_3 group[245]. In addition to isomerisation there is an exchange of halogen atoms between catalyst and chlorofluoroethane. The introduction into chloroethane of the trichlorosilyl group considerably accelerates the dehydrochlorination of chloroethanes under the action of $AlCl_3$.[246–249] The main direction of this reaction is intramolecular dehydrochlorination with the formation of silicon-containing alkenes[247]. For 2-chloroethylsilane, in addition to dehydrochlorination under the action of $AlCl_3$ there is appreciable elimination of $SiCl_4$.[250–252] This process can proceed with quantitative formation of $SiCl_4$[250] (scheme 24).

$$CH_2ClCH_2SiCl_3 \xrightarrow{AlCl_3} CH_2{=}CH_2 + SiCl_4$$
$$CH_3CHClSiCl_3 \xrightarrow{AlCl_3} CH_2{=}CHSiCl_3 + HCl\,. \qquad (24)$$

3. HIGHER CHLOROALKANES AND CHLOROCYCLOALKANES

Higher chloroalkanes, like chloroethanes, form complexes with halides of coordination-unsaturated metals[253–255] in which there is exchange of halogens between the chloroalkane and the salt[253,256–262]. It has been noted[253–255] that halogen exchange is greatly accelerated when hydrogen chloride is introduced into the reaction mixture.

Aprotic acids bring about various rearrangements of chloroalkanes[157,263,264]. The most frequently encountered rearrangement is the transfer of chlorine atoms from one carbon atom to another[254,255,265–270]. Here the chlorine is usually transferred to the carbon with the greatest number of substituents, that is, from a primary to a secondary to a tertiary. Thus, under the action of $AlCl_3$ propyl chloride is completely isomerised into isopropyl chloride[265]. It is assumed that such isomerisation proceeds by a pseudo-ionic mechanism in an intermediate five-membered complex[255].

Under the influence of aprotic acids, when heated in the liquid phase chloroalkanes readily lose hydrogen chloride[6,266,267,271–275]. Here the chloroalkanes with CCl_3 groups and also alkyl chlorides containing chlorine atoms at secondary and tertiary carbon atoms are usually dehydrochlorinated to alkenes[184,276–286]. Under the action of aprotic acids primary alkyl chlorides are either isomerised[254,255,265–274] into secondary and tertiary alkyl chlorides, which then lose hydrogen chloride intramolecularly, or react by intermolecular dehydrochlorination, which leads to the formation of higher-molecular-weight products[6,270–272]. Thus Friedel and Crafts obtained a dimeric compound (chlorodecane) from pentyl chloride[271,272]. On reaction with aprotic acids compounds with the CCl_3 group are ionised with the formation of carbonium ions[287–289], which are converted by different paths. When a proton is present at a neighbouring carbon atom it is removed and an alkene is formed[4,193,280,281,290]. In the absence of such a hydrogen atom the carbocation can react by the breaking of carbon–carbon bonds[193,290–292] (scheme 25):

$$CHCl_2CCl_2CCl_3 + AlCl_3 \rightleftarrows [CHCl_2CCl_2\overset{+}{C}Cl_2][\overline{AlCl_4}] \rightarrow CCl_2{=}CCl_2 + [\overset{+}{C}HCl_2][\overline{AlCl_4}]$$
$$[\overset{+}{C}HCl_2][AlCl_4] \rightarrow CHCl_3 + AlCl_3\,. \qquad (25)$$

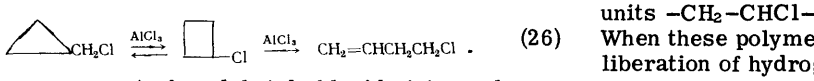
Perchlorinated alkanes with a long carbon chain (not less than C_5) are cyclised under the action of aprotic acids[30,293].

The main reaction of chloroalkanes in the presence of salts of coordination-unsaturated metals in the vapour

phase at 300–600°C is dehydrochlorination. In this the regularities which are observed in the liquid phase are retained. The dehydrochlorination of the long-chain chloroalkanes is accompanied by the isomerisation of the carbon skeleton[294], the transfer of the double bond along the carbon chain[295,296], and the breakage of a carbon–carbon bond, which leads to the formation of a mixture of alkenes. Completely chlorinated hydrocarbons are decomposed in the vapour phase under the action of Lewis acids with breakage of a C–C bond to give tetrachloroethylene and CCl_4.[297,298]

Chlorocycloalkanes. The conversions of 1,2,3,4,5,6-hexachlorocyclohexane and other chlorinated cyclohexanes have been studied in greatest detail. At moderate temperatures (20–120°C) the reaction of the chlorocyclohexanes with $AlCl_3$ is brought about by exchange of chlorine atoms between catalyst and chlorocyclohexane[299], by the migration of chlorine atoms in the cyclohexane ring[300] and by spatial isomerisation[299–301]. For example, under the action of $AlCl_3$ at 20°C *trans*-1,2-dichlorocyclohexane is partly converted into *cis*-1,2-dichlorocyclohexane and is isomerised to *cis*- and *trans*-1,4-dichlorocyclohexane. On heating γ-1,2,3,4,5,6-hexachlorocyclohexane to 112°C with $AlCl_3$ labelled with the isotope ^{36}Cl there is a vigorous exchange of chlorine isotopes between the catalyst and the hexachlorocyclohexane[299]. Furthermore, isomerisation of the γ-isomer into the α-isomer takes place[299–301]. It is noteworthy that when heated with aprotic acids all the isomers of hexachlorocyclohexane are converted into the α-isomer, the configuration of which is most favourable energetically[301]. At high temperatures (250–400°C) chlorinated cyclohexanes lose hydrogen chloride readily under the influence of aprotic acids[301–305]. Thus hexachlorocyclohexane is dehydrochlorinated in the presence of $FeCl_3$ with the formation of 1,2,4-trichlorobenzene and of its isomerisation product 1,2,3-trichlorobenzene[301]. Here the α-isomer is dehydrochlorinated with greater difficulty than the other hexachlorocyclohexane isomers.

Cyclobutyl chloride and cyclopropylmethyl chloride undergo initial conversions under the action of $AlCl_3$.[306] Cyclopropylmethyl chloride readily rearranges at −40°C into cyclobutyl chloride and 1-chlorobut-3-ene (scheme 26):

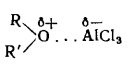


(26)

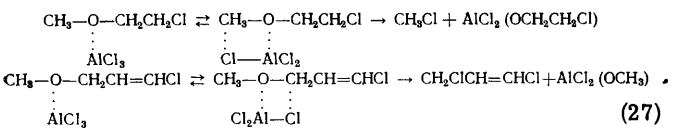
The rearrangement of cyclobutyl chloride into cyclopropylmethyl chloride and 1-chlorobut-3-ene takes place at a higher temperature (+15°C). Kinetic investigations[306] of these conversions show that the rearrangements have an ionic mechanism.

4. SUBSTITUTED CHLOROALKANES

Chloroalkanes which incorporate other halogens (fluorine or bromine) readily disproportionate in the presence of aprotic acids[266,307]. The introduction of alkoxy-groups into chloroalkanes accelerates their dehydrochlorination[308]. The reaction centre of alkoxychloroalkanes in their reaction with aprotic acids could be the ether group. Complexes of the type



are formed, which decompose when heated, with the formation of aluminium alkoxides and chloroalkanes[309]. The ether decomposes in such a way that the radical split off in the form of a halogenoalkane is that which has most tendency to acquire part of the positive charge from the oxygen atom. For example, when 2-chloroethyl methyl ether reacts with $AlCl_3$ it decomposes with liberation of methyl chloride[309], whereas 1,3-dichloro-prop-2-ene is formed from 3-chloroprop-2-enyl methyl ether[310] (scheme 27):



(27)

When the alkoxy-group in the chloroalkanes is in proximity to reactive CCl_3 or CHCl groups, which exhibit labile chlorine atoms, then the conversion of such compounds in the presence of aprotic acids leads to the formation of epoxy-compounds which are subsequently rearranged into ketones and acyl chlorides[311].

When γ- and δ-chlorine-containing ethers are heated with $FeCl_3$ or $SbCl_5$ they are cyclised with the formation of oxacycloalkanes[312–315]. For example, tetrahydrofuran and the metal chloride are formed in high yield from 4-chlorobutyl methyl ether in the presence of $FeCl_3$.[315]

Chloroalkanes which include phenyl groups readily undergo autocondensation under the conditions of the Friedel–Crafts reaction with release of hydrogen chloride and formation of cyclic and linear compounds[316–318]. Thus on heating a mixture of 1-chloro-1-phenylethane and $AlCl_3$ two molecules of the former are condensed and 9,10-dihydro-9,10-dimethylanthracene is obtained[312]. When in a chloroalkane there are 3–5 carbon atoms between the chlorine atom and the phenyl group, such compounds undergo cycloalkylation[319].

5. CHLORO-CONTAINING POLYMERS

The reactions of salts of coordination-unsaturated metals with polymers which are widely used in industry have been most studied. They include homopolymers and copolymers of vinyl chloride and vinylidene chloride and also chlorinated poly(vinyl chloride), which consist of the units $-CH_2-CHCl-$, $-CHCl-CHCl-$, and $-CH_2-CCl_2-$. When these polymers are heated they decompose with liberation of hydrogen chloride[320–323]. Many investigations devoted to the dehydrochlorination of poly(vinyl chloride) (PVC) showed that loss of hydrogen chloride takes place by ionic[322,324], pseudo-ionic[322,325], and radical[321–323] mechanisms. In the presence of salts of coordination-unsaturated metals the dehydrochlorination of PVC is accelerated[320–322,326–331] and proceeds by a pseudoionic mechanism[325,327,328]. Here the rate of dehydrochlorination is even greater when the salts of coordination-unsaturated metals and the hydrogen chloride liberated form rather stable complexes of the type MX.HCl,[322,332–334] which catalyse the decomposition of the polymer, owing to their acidic nature. The dehydrochlorination of PVC under the action of aprotic acids is effected both intramolecularly (which leads to a system of conjugated double bonds[335–338]) and also intermolecularly, as a result of which a structured, insoluble polymer is formed[339]. Furthermore, destruction of the PVC with breaking of the carbon–carbon bond is observed[340]. Organic solvents, such as dimethylformamide and aromatic amines, which form stable complexes with aprotic acids, decrease the catalytic action of these salts, as a result of which the rate of dehydrochlorination of PVC decreases considerably[341–343].

To suppress the dehydrochlorination of chlorine-containing polymers in their manufacture into various articles, stabilisers are usually employed. Salts of coordination-unsaturated metals are used as stabilisers for PVC [320,321,344,345]. They include aluminium, zinc, cadmium, and lead salts of stearic, lauric, caprylic, and other organic acids, and also the dicarboxylates of dialkoxides [320,321]. In addition, basic lead salts of organic and inorganic acids find wide application. The stabilising action of these salts is based on both the bonding of the hydrogen chloride released in the destruction of the polymers and on their reaction with the labile chlorine atoms of the polymer [346-349]. In the latter instance there is exchange of the chlorine atoms in the tertiary alkyl chloride and allyl chloride groupings which are present in commercial PVC [350], by the acyl residues of the salts [333,334,346-349,351] with the formation of ester groups (scheme 28):

$$-\overset{|}{\underset{|}{C}}\text{Cl} + Pb(OCOR)_2 \rightarrow -\overset{|}{\underset{|}{C}}\text{OCOR} + PbCl(OCOR). \qquad (28)$$

Since the sub-units which contain the ester groups are more stable thermally than the sub-units with labile chlorine atoms [352] the resistance of the polymer to dehydrochlorination is enhanced as a result of this reaction [333,334,351]. The stabilising action of certain salts of coordination-unsaturated metals is also based on the fact that they form complexes with reactive groups of the polymer (conjugated double bonds, oxygen-containing groups) which give it a colour [332-334]. As a result of complex formation by chromophoric groups with a stabiliser the colour of the polymer is reduced.

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Hence the principal reaction of hydrogen-containing organochlorine compounds under the action of aprotic acids is dehydrochlorination, which is intramolecular or intermolecular, depending on the structure of the initial organochlorine compound. Intramolecular elimination of hydrogen chloride takes place through the intermediate formation of relatively stable carbonium ions and leads to the formation of alkenes. Intermolecular dehydrochlorination is effected by simultaneous electron transfer to the transition complex, as a result of which a higher-molecular-weight compound is obtained. In the presence of $AlCl_3$ certain chloroethanes (dichloroethanes, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane) can give high yields of polymers with conjugated double bonds which exhibit semiconducting properties. Dehydrochlorination is usually accompanied by parallel processes, such as cationic polymerisation of chloroalkenes, isomerisation, rearrangements, disproportionation, halogen exchange between chlorine-containing compounds and the catalyst, cyclisation, complex formation, breaking of –C–C–, –C–O– and other bonds, dehalogenation, which mainly proceed by ionic or pseudoionic mechanisms. The conditions for the reaction of organochlorine aliphatic compounds with the salts of coordination-unsaturated metals have a marked effect on the direction of these reactions. As a result suitable choice of the reaction conditions enables certain of the above processes to occur preferentially and desirable products to be obtained in high yields.

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