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Chemical dehydrohalogenation of halogen-containing polymers

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ABSTRACT. This review is concerned with the dehydrohalogenation of halogen-containing polymers as a method of obtaining polymers with a system of conjugated multiple bonds. Different dehydrohalogenating agents are described and the mechanism, kinetics and structure of the reaction products are examined.

The bibliography includes 159 references.

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I. Introduction

Dehydrohalogenation of halogen-containing compounds has been studied in detail[1] in the field of organic chemistry and is widely used for the synthesis of unsaturated compounds.[2]

In the chemistry of macromolecular compounds the majority of studies on the dehydrohalogenation of halogen-containing polymers were carried out previously in order to find effective stabilisers for these polymers, in particular for poly(vinyl chloride) (PVC), because of their low resistance towards heat and light. A number of reviews have been devoted to the thermal degradation of PVC.[3–18]

Several methods for the dehydrohalogenation of halogen-containing polymers are known.[3] However, thermal and photodehydrohalogenation as well as dehydrohalogenation by means of X-radiation and γ-radiation result in the formation of cross-linked products with short sequences of conjugated multiple bonds. Dehydrohalogenation by chemical agents can give considerably longer segments of conjugation, particularly under mild conditions (at reduced temperatures).

At the beginning of the 1960's studies in which the directed dehydrohalogenation of halogen-containing polymers was investigated as a method of obtaining polymers that contain a system of conjugated multiple bonds in the main chain started to be published in the scientific literature. A considerable amount of experimental experience in this field of polymer-like reactions has been built up so far, but reviews devoted to the chemical dehydrohalogenation of polymers are absent from the literature. Therefore, the aim of the present reivew is to correlate the literature data on the dehydrohalogenation of halogen-containing polymers by different chemical agents and to examine the structure of the reaction products as well as the kinetics and mechanisms of the reactions that occur.

II. Dehydrohalogenation by alkalis

Alkali metal hydroxides, in particular those of Na and K, are widely used as dehydrohalogenating agents. However, aqueous solutions of NaOH and KOH only react effectively with halogen-containing polymers at high temperatures. Thus, for example, in order to dehydrochlorinate PVC completely with aqueous solutions of NaOH and KOH the reaction must be carried out at 250–270 °C.[19] At these temperatures the contribution from side reactions involving cross-linking and oxidation of the resulting sequences of conjugated double bonds increases considerably. At lower temperatures the reaction takes place extremely slowly. Thus, in the dehydrofluorination of poly(vinylidene fluoride) (PVDF) powder with an aqueous solution of NaOH at 90 °C for 5 h, there is only 7.8% elimination of HF.[20] Reactions with PVC [21] and vinylidene chloride–vinyl chloride copolymer[22] occurred in a similar manner.

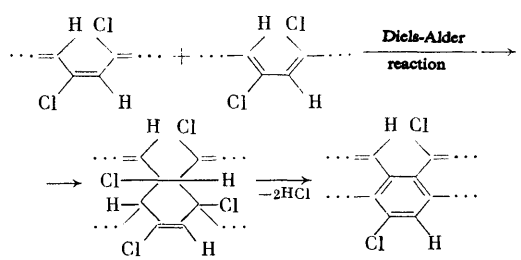
1. Dehydrohalogenation in the presence of phase-transfer catalysts

By using quaternary ammonium and phosphonium halides[20–27] and hydroxide[28] and also crown ethers[20,29] as phase-transfer catalysts it was possible to increase significantly the rate of alkaline dehydrohalogenation of halogen-containing polymers.

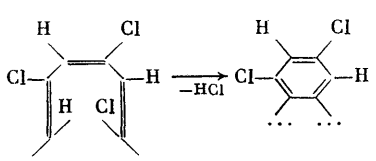
In a number of studies the dehydrohalogenation of PVC,[21,26,27] poly(vinylidene chloride) (PVDC),[29] PVDF,[20,23,25,28] and vinylidene chloride–vinyl chloride copolymer containing 5–20% of the latter (Saran)[22,24] was investigated. A high degree of conversion was achieved on average after 15–20 h at 60–100 °C, although data exists on the surface modification of PVDF films[23,25] and the dehydrochlorination of PVC [21] and Saran[22] that were carried out at room temperature. The reactions were conducted using powders,[20,21,24,27,28] films,[20,21,23–26] and solutions[22] of the polymers.

In the dehydrochlorination of PVC in the presence of quaternary ammonium or phosphonium halides,[21,26] black compounds are formed that undergo aerial oxidation and which have a conjugated polyene structure of the *trans*-polyacetylene type. As the reaction takes place, characteristic absorption bands appear in the IR spectra of the products due to isolated (1670 cm^{-1}) and conjugated (1560 cm^{-1}) C=C double bonds as well as an absorption band at 580 cm^{-1} attributed to bending vibrations of C–H bonds in *trans*-olefinic bonding.[21]

In the dehydrohalogenation of PVDC, Saran, and PVDF in the presence of onium salts, the reaction products are black powders or films that have the halogen-substituted polyene structure $-(-CX=CH-)_n-$, (X = Cl, F) and are stable towards aerial oxidation,[20,24] in contrast to dehydrochlorinated PVC.[21] In the IR spectra of the products from the dehydrohalogenation of poly(vinylidene halides) intense absorption bands occur in the region of 1600 cm^{-1} which correspond to stretching vibrations of conjugated C=C double bonds, and much less intense bands appear in the region of 2170 cm^{-1} that are attributed to the stretching vibrations of C≡C triple bonds which can be formed by the elimination of two molecules of hydrogen halide from a single vinylidene unit of the polymer.[20,22,24,29] In addition to that, in the IR spectra of the dehydrohalogenation products of these polymers, absorption bands have been recorded in the region of 865 and 3400 cm^{-1} that are attributed to aromatic structures and OH groups respectively. According to the authors of two studies,[24,29] aromatisation of the polyene sequences can occur via a Diels–Alder reaction followed by dehydrohalogenation of the resulting cyclohexene structures:



or as the result of intramolecular cyclisation via 1,6-elimination:



The authors attribute the low content of C≡C triple bonds in the dehydrohalogenation products at high degrees of conversion to aromatisation of the polyene sequences. Hydroxyl groups occur in the polymer as a result of nucleophilic substitution of the halogen atoms in the polymer by the hydroxyl ion.[24]

In the IR spectra of the dehydrohalogenation products with a high degree of conversion the absorption bands characteristic of the initial polymers have become very weak.

In several studies[20–22,24] a wide range of quaternary ammonium and phosphonium halides were used as phase-transfer catalysts; these differed according to the number of carbon atoms in the hydrocarbon substituents on the nitrogen or phosphorus atom—from tetramethylammonium bromide to an Adogen catalyst [trialkylmethylammonium (C_8-C_{10}) chlorides]. The activity of the onium salts in dehydrohalogenation reactions depends mainly on the number of carbon atoms in the catalyst molecule and is limiting in nature. For the dehydrohalogenation of PVC and PVDF the reaction occurred more rapidly and the conversion reached a maximum when tetrabutylammonium bromide (TBAB) was used as the catalyst. In the dehydrochlorination of Saran the best catalyst proved to be tetrapropylammonium bromide (TPAB). Similar results were obtained when the analogous phosphonium salts were used.

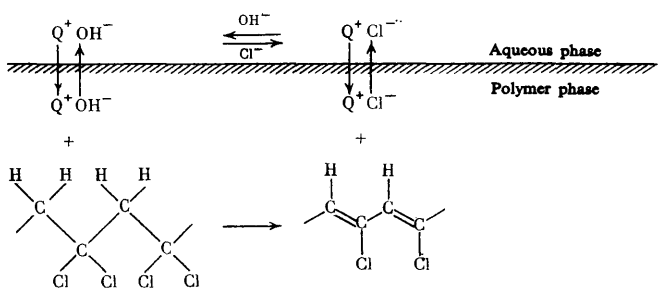
The limiting dependence of the activity of the catalyst on the number of carbon atoms in the substituents is accounted for using the concept of the hydrophile-lipophile balance (HLB). An increase in the lipophilic nature of the catalyst assists the reaction up to a given maximum. With a further increase in the number of carbon atoms the alkyl substituents of the catalyst inhibit its diffusion into the polymer. In two-phase aqueous organic reactions the negatively charged bases form ion pairs with the positive onium ions and are then extracted into the organic phase, where reaction takes place. Since exchange of anions at the phase boundary or in the aqueous phase occurs much more rapidly than the reaction between an ion pair and substrate (polymer), the rate of reaction mainly depends on the concentration of catalyst in the organic phase.[21] In the dehydrohalogenation of polymers a layer of reaction products that are insoluble is formed on their surface, significantly inhibiting diffusion of the dehydrohalogenating agent into the polymer, i.e., the reaction is self-inhibited.[25]

For a quantitative determination of the HLB the use of function D was proposed:

$$D = (\delta - \delta_w)^2/(\delta - \delta_o)^2,$$

where δ, δ_w, and δ_o are the solubility parameters of the onium salts, water (δ_w = 23.4) and the organic phase (polymer) respectively.[30] The catalytic activity of the onium salts increases with a decrease in the value of D,[24] in other words, it depends on the affinity of the ion pair for the organic phase (polymer), where dehydrohalogenation occurs. In the dehydrochlorination of Saran, TPAB had the greatest activity (higher and lower analogues were less active),[24] while in the dehydrohalogenation of PVC and PVDF, TBAB proved to be the most active.[20,21] This difference can be attributed to the more hydrophilic nature of PVDC compared to PVC and PVDF, which have similar solubility parameters.[20]

The mechanism of the dehydrohalogenation of PVDC under heterogeneous conditions in the presence of a phase-transfer catalyst (Q^+Cl^-) has been schematically represented.[24]



The ammonium hydroxide formed in the aqueous phase reacts with the polymer on the surface of the polymer particles according to an E_2 mechanism.[1] Molecules of Q^+OH^- penetrate the polymer phase and react with counterions of PVDC.

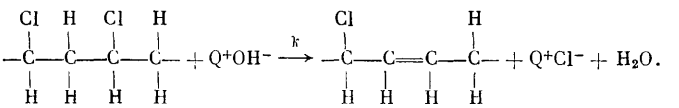
However, the empirically derived expression for the rate of dehydrochlorination of PVC [27] cannot be accounted for using this simple mechanism

$$v = k.[TBAB]^{0.43}.[NaOH]^{1.1},$$

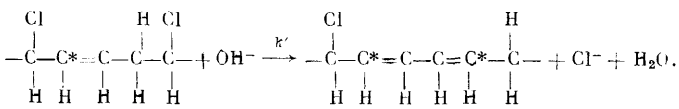
where [TABA] and [NaOH] are the concentrations of tetrabutylammonium bromide and alkali respectively. Therefore, Howang et al.[27] proposed the following mechanism of dehydrohalogenation that includes several stages in the case of PVC.

The initiation stage involves the elimination of HCl catalysed by a quaternary onium base (Q^+OH^-) with the formation of isolated

double bonds in the PVC chains

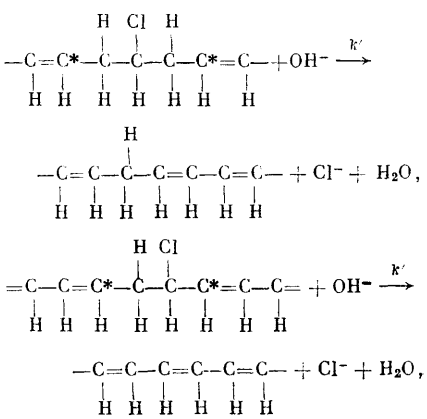


In the stage involving growth of the chain of conjugation, a vinyl chloride unit adjacent to a double bond in the presence of the OH^- anion readily loses HCl to form conjugated double bonds

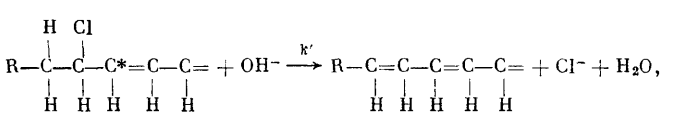


The carbon atoms of the extending conjugation front are marked with an asterisk.

In the termination stage elimination stops when two conjugation fronts in the same polymer chain meet



or when the end of the chain is reached by the front



where R are terminal groups of PVC.[27]

Dehydrohalogenation of halogen-containing polymers is assumed[21,24,26,27] to occur by a chain mechanism (zip process), according to which the isolated and conjugated double bonds in the polymer macromolecule activate the hydrogen and chlorine atoms in the α-position by increasing their activity and capacity to undergo elimination (allylic activation).

An expression for the rate of dehydrochlorination of PVC has been derived theoretically[27]

$$v = d[Cl^-]/dt = A^{1/2}[TBAB]^{1/2}[CH_2-CHCl]^{1/2}[OH^-],$$

where

$$A = k' \cdot k \cdot k_e \cdot K/(1+K) \cdot (k_e[OH^-] + k \cdot [CH_2-CHCl]);$$

$$K = [Q^+]_T/[Q^+]_p —$$

is the HLB coefficient; k' and k are the rate constants of the fundamental stages of dehydrochlorination; k_e is the rate constant of anionic exchange at the polymer–solution phase boundary; $[Q^+]_s$ and $[Q^+]_l$ are the concentrations of catalyst in the solid phase and in solution respectively. This expression correlates well with the experimentally determined value, which provides support for this mechanism.

It should be noted that when the dehydrohalogenation of polymers is carried out in solution with agitation, a precipitate of partially dehydrohalogenated polymer rapidly forms and the reaction continues in a similar manner to the reaction with powder. In the absence of agitation, when the organic phase is a solution of polymer, the activity of the catalyst depends on the organic solvent. Thus, in the dehydrochlorination of Saran in tetrahydrofuran (THF) solution the most effective catalyst proved to be TBAB,[22] whereas for solid Saran (powders and films) TPAB was more effective.[24] This difference in catalytic activity in the dehydrochlorination of solid Saran and its solution in THF can be attributed to the different solubility parameters of the solid copolymer (δ = 13.4) and THF (δ = 9.32).[22] For PVC, δ = 9.4–10.8.[24] When *o*-dichlorobenzene was used as the solvent, the dehydrochlorination of Saran was almost completely suppressed, while when 1,4-dioxan was used the reaction was faster than in THF.[22]

The degree of conversion in the aqueous alkaline dehydrohalogenation of polymers also depends on the concentration of catalyst and alkali and on the reaction temperature. When the concentration of catalyst is increased, conversion increases to a given level, after which it remains unchanged. This type of dependence is related to the fact that at high concentrations of catalyst a portion of it separates out from the aqueous phase to form an oily layer—it becomes a three-phase system. Therefore, the effective concentration of catalyst in the aqueous phase remains unchanged. At high concentrations of alkali a third phase of catalyst is also formed, and the dependence of conversion on the concentration of alkali with a constant concentration of catalyst is in the form of a curve with a maximum. At first, as the concentration of alkali in the aqueous phase increases, the conversion increases and reaches a maximum value, after which it starts to decrease. The drop in conversion is due to a decrease in the effective concentration of catalyst in the aqueous phase on increasing the concentration of alkali.[20–22,24]

In the dehydrochlorination of Saran in THF solution, KOH proved to be a more effective dehydrochlorinating agent than NaOH under the same reaction conditions. An increase in the concentration of Saran in THF solution led to a decrease in conversion, since the increase in viscosity of solution inhibited diffusion of ammonium hydroxide into the organic phase.[22]

The dependence of conversion on reaction temperature in the dehydrochlorination of PVC is limiting in nature with a maximum at about 70 °C. On increasing the temprature from 70 to 90 °C, the degree of conversion falls sharply. Initially this phenomenon was attributed to decomposition of the onium salts in alkaline solution at temperatures above 70 °C,[21] but more recent studies[20,24] have demonstrated that in the dehydrohalogenation of Saran and PVDF the degree of conversion increases with an increase in temperature even up to 110 °C. Therefore, the limiting dependence of conversion on temperature in the dehydrochlorination of PVC is attributed[24] to a change in the physical properties of the polymers at temperatures above the glass-transition temperature of PVC (about 80 °C), which can lead to a reduction in porosity of the PVC particles and a decrease in the rate of diffusion of the ammonium hydroxide into the polymer, in other words, there is a decrease in the overall rate of reaction.

In one study[28] in order to create milder conditions in carrying out the dehydrofluorination of PVDF, tetrabutylammonium hydroxide in a solution of t-butyl alcohol was used directly as the

dehydrohalogenating agent, as a result of which it was possible to avoid scissions of the polymer chain and obtain a fluorine-substituted polyacetylene structure on the surface of PVDF.

Crown ethers constitute another class of phase-transfer catalysts that are used in the dehydrohalogenation of halogen-containing polymers. The use of 18-crown-6 and dibenzo-18-crown-6 in the dehydrochlorination of PVC with aqueous solutions of NaOH or KOH proved ineffective.[21] In the aqueous alkaline dehydrofluorination of PVDF the catalytic activity of 18-crown-6 proved to be much lower than that of TBAB; while an attempt to use the more lipophilic dibenzo- and dicyclohexyl-18-crown-6 was unsuccessful because of the low solubility of the latter in the aqueous phase.[20]

However, when the dehydrochlorination of PVDC was conducted in the presence of 18-crown-6 in benzene, the reaction took place rapidly up to high degrees of conversion.[29] Dehydrochlorination was carried out in the three-phase systems: PVDC (film) + benzene + 18-crown-6 + KOH (pellets) and PVDC (film) + benzene + 18- crown-6 + KF/CaO. The degrees of conversion for systems with KF/CaO and KOH were similar, but the concentration of the crown complex with KF/CaO was 6 times lower than the concentration of the crown complex with KOH because of its low solubility in benzene. Hence it may be concluded that the system KF/CaO – 18-crown-6 is more effective in the dehydrochlorination of PVDC films in benzene.

At 80 °C after 1 h, elimination of 0.97 chlorine atoms on average per monomer unit with the formation a chlorine-substituted polyene structure has occurred. When dehydrochlorination is carried out for a more prolonged period further elimination of HCl occurs, and after 14 h 1.6–1.7 chlorine atoms are eliminated on average per monomer unit.

In the IR spectra of the dehydrochlorination products absorption bands are detected at 2170 cm^{-1} and at 866 and 755 cm^{-1}, which are attributed to stretching vibrations of C≡C triple bonds and bending vibrations of C–H bonds in aromatic structures respectively. When KOH is used in the dehydrochlorinating system, mainly C≡C triple bonds are formed at high degrees of conversion, while when KF/CaO is used aromatic structures are mainly formed by the above-mentioned Diels–Alder and intramolecular 1,6-elimination types of reaction, which can be illustrated by the ratio of intensities of the absorption band at 2170 cm^{-1} to those at 866 and 755 cm^{-1}. Thus, for the system with KOH, $I_{2170}/(I_{866} + I_{755}) = 1.2$, while for the system with KF/CaO, $I_{2170}/(I_{866} + I_{755}) = 0.3$.[29]

The rate of dehydrochlorination depended to a considerable degree on the reaction temperature. While 0.97 chlorine atoms were eliminated on average per monomer unit at 80 °C, when the reaction was carried out at 20 °C only 0.15 atoms were eliminated.[29]

2. Dehydrohalogenation by alcoholic solutions of alkalis

Treatment of halogen-containing compounds with alcoholic solutions of alkali metal hydroxides is a traditional method of dehydrohalogenation that has been used in both organic chemistry and polymer chemistry.

A number of studies have been devoted to the dehydrohalogenation of PVC,[31–33,35,43,44,55,57] PVDC,[36–38,41,42,45,56] PVDF,[40–42] poly(vinylidene bromide) (PVDB),[41,42] and also a polymer that had the structure of poly(1,2-dibromoethylene), obtained by the dehydrochlorination and subsequent bromination of PVC.[55]

When the dehydrohalogenation of halogen-containing polymers is carried out in solution, with other conditions being equal the rate of reaction depends on the polarity of the solvent. Thus, when the dehydrochlorination of PVC is carried out in dimethylformamide (DMF) solution, the rate of reaction, the conversion, and also the length of the resulting polyenes were considerably greater than when the reaction was carried out in THF solution.[31,32]

In the IR spectra[31,33] of the dehydrochlorination products of PVC there are absorption bands at 1005 cm^{-1} and 3010 cm^{-1} which are characteristic of bending and stretching vibrations respectively of C–H bonds in long *trans*-polyenes.[34] In the Raman spectra intense lines occur in the region of 1100 and 1500 cm^{-1} that are typical for stretching vibrations of carbon–carbon single and conjugated double bonds respectively.[35]

At degrees of conversion of 50–60%, the length of the polyene sequences formed in PVC macromolecules under the experimental conditions reaches a maximum value (about 40 conjugated C=C bonds), and then as dehydrochlorination progresses it decreases.[31,32] Bowley et al.[31,32] account for this phenomenon as follows. At degrees of conversion up to 50–60%, the long conjugated polyenes formed in the PVC macromolecules are separated by sections of unreacted polymer. These sections of the initial polymer sterically shield the polyene sequences from interchain cross-linking.[31] As dehydrochlorination progresses the unreacted sections disappear and at the same time there is an increased probability of cross-linking on the double bonds with scission of the chain of conjugation and a decrease in the length of the polyenes.[32] In fact, in the IR spectra of completely dehydrochlorinated PVC absorption bands occur at 2845 and 2920 cm^{-1} that are characteristic of stretching vibrations of C–H bonds in saturated structures.[32]

It should be noted that the degree and rate of dehydrochlorination and also the structure of the reaction products does not depend on the tacticity of the initial polymer.[31,32]

The dehydrochlorination of PVDC powder has been investigated in three studies.[36–38] The highest visually recorded rate of reaction was reached when a solution of KOH in isopropyl alcohol was used as the dehydrochlorinating agent. Solutions of LiOH and NaOH in methanol and ethanol proved less effective. The reaction was carried out at room temperature. Since no absorption bands characteristic of conjugated dienes and trienes were detected in the IR spectra of the intermediates, the authors conclude that elimination of HCl does not occur randomly at the same time in several sites of many macromolecules but has the form of a chain reaction.[36] After the first 4 h more than half of the initial chlorine content has been eliminated from the polymer. For complete elimination of chlorine 40–50 h is required.[37,38] In the IR spectra of the reaction products there is a rapid increase in a broad absorption peak at 1630 cm^{-1}, attributed to C=C double bond vibrations, which is shifted to 1590 cm^{-1} when the reaction is continued in excess of 12 h. The authors attribute this shift to a change in the environment of the carbon atoms from aliphatic (1630 cm^{-1}) to aromatic (1590 cm^{-1}). In the IR spectra of the reaction products there are also absorption bands at 1720 and 3440 cm^{-1}, attributed to vibrations of O=C< and OH groups respectively.[36,38] The authors account for the absence of absorption bands characteristic of C≡C triple bond vibrations in the IR spectra of the dehydrochlorination products of PVDC by the fact that at the first stage of the reaction the resulting chlorine-substituted polyene structures $-(-CH=CCl-)_n-$ react with each other by a Diels–Alder-type reaction (see above). Subsequent dehydrochlorination of the reaction products results in the formation of aromatic structures.[36,38] According to the dehydrochlorination mechanism put forward by Barton et al.[38] elimination of HCl from the polymer chain occurs via the formation of an ether in a

Williamson reaction[39] followed by the elimination of a molecule of isopropyl alcohol and the formation of a C=C double bond.

In the dehydrofluorination of PVDF both at room temperature[40] and at 50–100 °C [20] by a solution of KOH in isopropyl alcohol, in addition to absorption bands in the IR spectra of the reaction products at 3400, 1580, and 1100 cm^{-1} that are characteristic of OH groups, conjugated double bonds (C=C), and C–O–C ether bonds respectively, there is an absorption band in the region of 2050–2200 cm^{-1}, attributed to stretching vibrations of C≡C triple bonds.

The dehydrohalogenation of poly(vinylidene halides) (PVDF, PVDC, and PVDB) by a mixture of a saturated solution (25 wt.%) of KOH in ethanol and THF has been studied.[41,42] By using THF in the mixture it is possible to carry out dehydrohalogenation under mild conditions—at room temperature and below—because of its specific solvating nature and complexing ability, which reduces to a minimum the contribution of side reactions involving cross-linking, degradation, and nucleophilic substitution of halogen atoms by hydroxyl and ethoxy groups. It should be noted that addition of certain polar solvents [dimethyl sulphoxide (DMSO),[43,44] pyridine[45]] to an alcoholic solution of alkali resulted in an appreciable acceleration of dehydrohalogenation of PVC and PVDC. Solvation of the alkali metal cation with THF molecules increases the reactivity of the hydroxyl ion, which assists the dehydrohalogenation reaction.[41,42] The role of THF involves not only its catalytic effect on the elimination of hydrogen halide but also changing the conditions of interaction in the system polymer–reactive medium. This manifests itself in the swelling of polymers in THF, which assists the diffusion of dehydrohalogenating agent into the polymer. The optimum ratio of the components of the dehydrohalogenating mixture, in which the maximum rate of reaction and degree of dehydrohalogenation are achieved, is: 40 wt.% alcoholic solution of KOH + 60 wt.% THF.[41,42]

The theoretical reaction scheme of the dehydrohalogenation of poly(vinylidene halides) can be shown as follows:[41]

$$-(-CH_2-CX_2-)_n- \xrightarrow[-nHX]{} -(-CH=CX-)_n- \xrightarrow[-nHX]{} \longrightarrow -(-C\equiv C-)_l- \ldots =(=C=C=)_m=,$$

where $l + m = n$ and X is a halogen.

A feature of the dehydrohalogenation of polymers under heterogeneous conditions is that the rate of reaction depends not only on the strength of the carbon–halogen bond but also on the rate of diffusion of the dehydrohalogenating agent into the polymer substrate.[41] Therefore, the reaction occurs much more rapidly with powders than with films because of the degree of dispersion and highly extended surface of powders. Thus, the dehydrohalogenation of PVDF powder at room temperature was complete after 10 h, that of PVDC was complete after 1 h, and that of PVDB after 30 min.[41,42] The dehydrohalogenation of PVDF and PVDC films takes place much more slowly. An increase in reaction temperature results in a marked acceleration of dehydrohalogenation. In addition to the accelerating effect of heat on the chemical reaction this is also due to swelling of the polymers in THF, which assists diffusion of the reactants. In all, poly(vinylidene halides) can be arranged in the following order with respect to their rate of dehydrohalogenation: PVDB > PVDC > PVDF.[41]

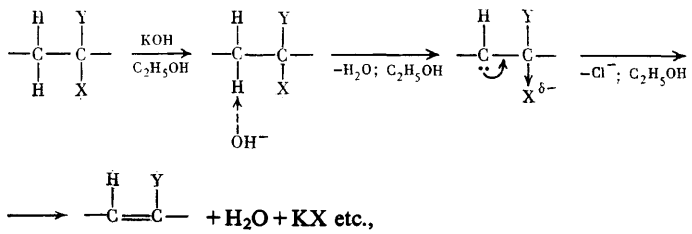
As the dehydrohalogenation of poly(vinylidene halides) takes place, in the IR spectra of the reaction products the absorption bands that are characteristic of vibrations due to the carbon–halogen bond over the frequency range 400–800 cm^{-1} disappear and new absorption bands appear in the region of 1600 cm^{-1} (very strong) and 2170 cm^{-1}, which are attributed to stretching vibrations of carbon–carbon double and triple bonds respectively.[41,42] A change of reaction temperature from –10 °C to 68 °C did not produce any appreciable change in the relative intensities of these bands. However, according to electronic Auger spectroscopy data, when the reaction is carried out at room temperature the dehydrochlorination products of PVDC contain about 15% cross-linked graphite-like structures, whereas at a lower temperature (–10 °C) products with a linear (one-dimensional) structure are formed. Evsyukov et al.[41,42] resolve the inconsistency between the IR and Auger spectroscopic data by assuming that in the chemical dehydrohalogenation of poly(vinylidene halides) a cumulene modification of carbyne (β-carbyne) is formed, and absorption of the cumulene structure appears in the region of 1600 cm^{-1}. This accounts for there being no differences in the IR spectra of poly(vinylidene halides) dehydrohalogenated at different temperatures since absorption of conjugated and isolated C=C double bonds also appears at about 1600 cm^{-1}.[46] It should be noted that previously the absorption band in the region of 2100–2200 cm^{-1} in the IR spectra of carbyne was attributed to vibrations due to polyyne structures while the band in the region of 1600 cm^{-1} was attributed to C=C double bond vibrations formed as a result of interchain cross-linking.[45,47] In order to confirm the validity of assigning the absorption bands in the region of 1600 cm^{-1} in the IR spectra to vibrations of cumulated double bonds of β-carbyne, a numerical calculation of the inherent vibrational frequencies of a cumulene chain was carried out,[48] taking into account ideas about the zigzag nature of a carbyne chain,[49,50] which at the present time have been experimentally confirmed.[51,52] The results of the calculation are in good agreement with the experimental IR spectra of the dehydrohalogenation products of poly(vinylidene halides).

By studying the electronic structure of the dehydrohalogenation products of poly(vinylidene halides) using Auger spectroscopy and also electron characteristic energy loss spectroscopy, it was possible to obtain complete confirmation of their one-dimensional cumulene structure.[41,42] On the curve of density of the valence states of dehydrochlorinated PVDC there are three well-defined maxima at energies of 16, 19, and 25 eV, which relate respectively to the base of the π-sub-band and the ceiling and base of the σ-sub-band. This position of the maxima on the energy scale is typical for linear structures and is in good agreement with the results of a calculation of the density distribution of states in the valence band of carbyne.[53] The position of the base of the π-sub-band at 16 eV is a clear indication of the cumulene nature of the bonds in the dehydrohalogenation products. The threshold of the loss function in the electron characteristic energy loss spectrum, which corresponds to the width of the optical forbidden band, is equal to 1 eV, which is also consistent with the results of calculation of the electronic spectrum of cumulene chains.[41,42]

In the Raman spectra of the dehydrohalogenation products of poly(vinylidene halides), two lines occur at about 1550 and 2150 cm^{-1}, corresponding to stretching vibrations of cumulated C=C double bonds in the polymer chain.[54] On increasing the wavelength of exciting light from 457.9 to 647.1 nm, the positions of the lines are shifted to lower frequency, which suggests that there are chain distributions according to the effective lengths of conjugation in the carbyne obtained.

An ionic mechanism has been proposed[41,42,55] for the dehydrohalogenation of halogen-containing polymers by an alcoholic

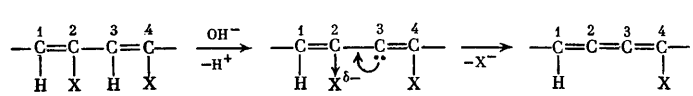
solution of alkali that is similar to the well-known mechanism in organic chemistry for the dehydrohalogenation of alkyl halides by bases.[1] According to this mechanism a hydroxide ion removes a proton from the chain of the initial polymer, leaving a free electron pair in its place. The halogen atoms on the neighbouring carbon atom acquire a partial negative charge as a result of the inductive effect and are readily detached by (alcohol) solvent molecules. The eliminated halogen ion is bound in solution to an alkali metal cation



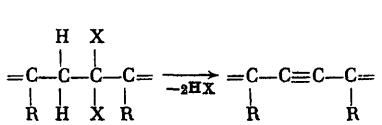
where X = Y is a halogen[41,42] or Y = H.[55]

Subsequent elimination of hydrogen halide from the units that are adjacent to the resulting double bond occurs with greater ease than for the initial polymer because of the allylic activation effect.[55]

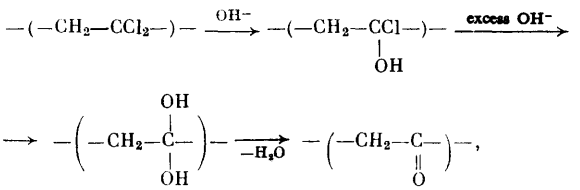
Using this mechanism, Evsyukov et al.[41,42] account for the formation of β-carbyne in the dehydrohalogenation of poly(vinylidene halides) in the following manner. At the first stage of the reaction a halogen-substituted polyene structure $-(CH=CX)_n-$ is formed. After removal of a proton from the resulting structure, a free electron pair is left in its place, according to the above mechanism. This pair causes a shift in electron density from the C(3) atom to the C(2) atom because the double bond between the C(3) and C(4) atoms prevents a shift in electron density to the C(4) atom. As a result of the redistribution of electron density the halogen atom on the C(2) carbon atom acquires a greater negative charge than the halogen atom on the C(4) carbon atom. As a result, elimination of a halogen ion actually takes place from the C(2) atom to form a cumulene structure.



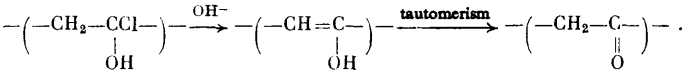
The C≡C triple bonds whose existence is indicated by the absorption band in the region of 2100–2200 cm^{-1} in the IR spectra of β-carbyne obtained by dehydrohalogenation of poly(vinylidene halides) occur as defect units in relation to the final cumulene structure. They can be formed by the elimination of two hydrogen halide molecules from the monomer units that occur in the polymer macromolecules between defect units[41,42]



These defects can comprise branching and "head-to-head" structures in the initial polymer as well as defects formed by side reactions involving cross-linking, oxidation, degradation, and nucleophilic substitution of halogen atoms by hydroxyl and alkoxy groups. The occurrence of hydroxyl groups in the polymer chain can lead to further side reactions[56]

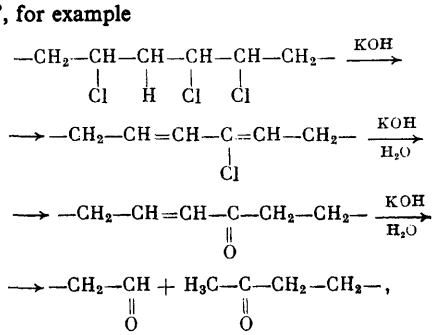


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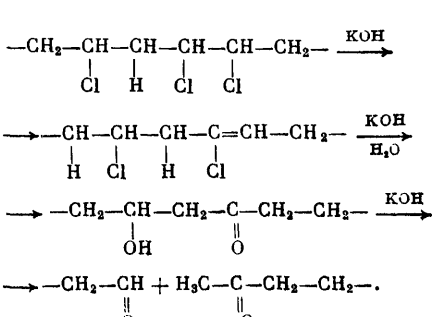


In a study[57] of the reaction between PVC and alkali, particular attention was given to the degradation of PVC with scission of the polymer chain. The reaction of PVC with an alcoholic solution of KOH was carried out in THF solution under specially selected conditions in order to prevent the rapid loss in solubility and precipitation of the polymer from solution. It was shown by Schwenk[57] that the Fikentscher coefficient determined by viscometry, which decreases during the reaction over a period of 90 min to 2/3 of its original value in the initial polymer, is not a reliable criterion of molecular weight in the case of branched polymer structures that are formed through side reactions involving cross-linking. For a more detailed study the author used gel permeation chromatography (GPC). However, in this case also a determination of the true molecular-weight distribution is made difficult by the presence of a colloidal fraction with intermolecular cross-linking in the solution of reaction products, which passes through a conventional filter but settles in a chromatographic column. Nevertheless, the GPC data clearly indicate the presence of a low-molecular weight fraction in the reaction products of PVC and KOH that is absent in the initial polymer.

From the analysis of model reactions Schwenk[57] has proposed different variants of the mechanism of the degradation of PVC with scission of the polymer chain by an alkali. In the opinion of Schwenk, it is most likely that degradation occurs at those sites of the polymer chain in which the monomer units are joined "head-to-head", for example



or



A reduction in the temperature of dehydrohalogenation leads to a decrease in the proportion of side reactions. Thus, for example, on treatment of a solution of PVC in THF with a solution of KOH in methanol at 60 °C, the reaction products contained 10 oxygen atoms for every 100 vinyl chloride units, whereas when the reaction was carried out at room temperature this was reduced to 2 oxygen atoms.[57]

A kinetic equation for the concentration of the polyenes formed by dehydrochlorination of PVC was derived by Shindo and Hirai[55]

$$[P_n] = K_n \cdot t^n,$$

where $[P_n]$ is the concentration of polyenes from n conjugated double bonds; t is the reaction time;

$$K_n = (1/n!)k_1k_2 \ldots k_n[KOH]^n.[PVC],$$

where $k_1, \ldots, k_n$ are the rate constants of the fundamental elimination reactions; [KOH] and [PVC] are the concentrations of KOH and PVC respectively.

A kinetic equation for the total concentration [E] of double bonds in the dehydrochlorination products of PVC was derived by Östensson and Flodin[44]

$$dE/dt = k_1([PVC]_0 - [E])([KOH]_0 - [E]),$$

which after integration gives

$$(1/\ln 10)([PVC]_0 - [KOH]_0).k_1t + \lg([PVC]_0/[KOH]_0) =$$

$$= \lg\{([PVC]_0 - [E])/([KOH]_0 - [E])\}.$$

In this case $[PVC]_0$ and $[KOH]_0$ are the initial concentrations of PVC and KOH respectively.

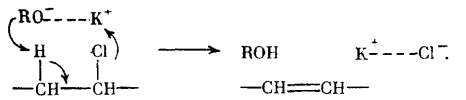
III. Dehydrohalogenation by alkali metal alkoxides

Alkali metal alkoxides (principally potassium t-butoxide) are used as widely as alkalis in the dehydrohalogenation of halogen-containing polymers. In a number of studies the dehydrohalogenation of PVC,[31,32,58–66] chlorinated PVC (CPVC),[65] PVDC,[56,66] and PVDF [40] by potassium t-butoxide[31,32,40,56,58–64] and sodium amoxide[65,66] was investigated.

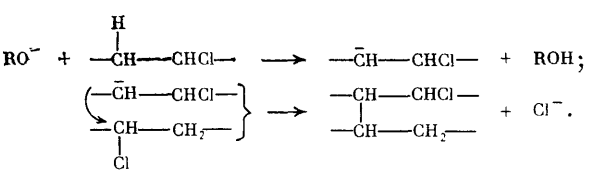
When potassium t-butoxide (t-C_4H_9OK) the KOH were used as the dehydrochlorinating agent under the same conditions, the rates and degrees of dehydrochlorination of PVC were similar. However, when t-C_4H_9OK is used, much longer polyene sequences (more than 65 conjugated C=C bonds) are formed than when KOH is used under the same conditions (about 40 units).[31,32] The rate and degree of dehydrohalogenation increase with an increase in polarity of the solvent.[31,32,56]

A study[61] of the dehydrochlorination of PVC by t-C_4H_9OK using GPC and UV spectroscopy showed that at the early stages of the process, macromolecules appear in the reaction products with a molecular weight similar to that of the initial polymer but containing short polyene residues (P_2 products). The concentration of such macromolecules (P_2) increases up to a degree of conversion of 10% and remains unchanged up to a degree of dehydrochlorination of 20%. Then, as the reaction progresses the concentration of P_2 decreases and is reduced to zero when the degree of conversion is 100%. Starting from a degree of dehydrochlorination of 4%, P_1 macromolecules appear in the reaction products with a molecular weight higher than the initial PVC and containing long polyene sequences. The concentration of P_1 increases as the reaction continues right up to complete dehydrochlorination. At advanced stages of dehydrochlorination, a small number of P_3 polyene macromolecules appear in the reaction products with a low molecular weight (200–800), which are formed as a result of side reactions involving chain scission.[61] Thus, products P_2, which are formed at the early stages of dehydrochlorination by elimination of several HCl molecules from the macromolecules of the initial PVC, as the reaction progresses undergo a further conversion to form products P_1 with a higher molecular weight than that of the initial polymer and containing long polyene sequences. Products P_1, in turn, partly undergo alkaline degradation to form products P_3 with a low molecular weight but containing long polyene sequences.

Elimination of HCl by the action of t-C_4H_9OK in pure THF is an ion pair reaction with the simultaneous removal of a proton and Cl^- anion:



This accounts for the solubility (lack of cross-linking) of the reaction products at high degrees of conversion. Some increase in the molecular weight of the reaction products relative to the initial PVC is attributed by Dussoubs et al.[61] to association of polyconjugated macromolecules without the formation of chemical cross-linked structures. In the opinion of the authors, when alcoholic solutions of bases (alkoxides or alkalis) are used, elimination of HCl occurs by an ionic mechanism through solvation of Cl^- anions with alcohol molecules, which makes side reactions involving cross-linking possible:



When the reaction is carried out in the presence of oxygen, the products of the complete dehydrochlorination of PVC are soluble in polar solvents.[62] However, the presence of oxygen leads to a reduction in the rate of dehydrochlorination and in the length of the resulting polyene sequences, which is due to the formation of a stable ternary complex of THF–oxygen–PVC, that has an affect on the subsequent course of the reaction.[63] When the dehydrochlorination of PVC is carried out in an atmosphere of argon, products with a polyacetylenic structure that are close in composition to the formula $(CH)_x$ are formed,[62] whereas for the dehydrochlorination product in an atmosphere of argon/oxygen (50% O_2) the formula $(CHO_y)_x$, where $y = 0.0032$, was established.[63]

The vibrational spectra of the dehydrohalogenation products of PVC, PVDC, and PVDF by treatment with t-C_4H_9OK are similar to the spectra of the dehydrohalogenation products of the corresponding polymers from treatment with alkalis,[31,32,40,56,62] as described above in Section II. However, when CPVC and PVDC are dehydrochlorinated with sodium amoxide, chlorine-substituted polyene (chlorovinylene) structures are formed,[65,66] further dehydrochlorination does not occur, and in the IR spectra of the reaction products where is no absorption band in the region of 2100–2200 cm^{-1} characteristic of stretching vibrations of C≡C triple bonds. Moreover, during the dehydrochlorination of CPVC by sodium amoxide, a side reaction involving alkoxylation occurs,[65]

whereas in the dehydrochlorination of PVC by t-C_4H_9OK side reactions involving substitution were not observed.[60]

It was shown by Bowley et al.[31,32] that the rate and degree of dehydrochlorination of PVC as well as the structure of the reaction products do not depend on the tacticity of the initial polymer. However, it was concluded by Martinez et al.[64] from UV spectroscopic data that at the early stages of dehydrochlorination of PVC, elimination of HCl occurs selectively in isotactic and heterotactic triads. In the case of a *gauche* conformation in these triads, elimination occurs by a *syn* mechanism to give *cis* double bonds.

It should be noted that t-C_4H_9OK prepared directly during dehydrohalogenation exhibits considerably greater activity in the elimination of hydrogen halide than that prepared earlier. Thus, when tertiary butyl alcohol and metallic potassium are added to a solution of PVC in THF, on carrying out the reaction for 2 h at 60–65 °C the degree of dehydrochlorination reaches 95%, whereas when previously prepared t-C_4H_9OK is used under the same conditions only 30% dehydrochlorination is achieved.[67]

IV. Dehydrohalogenation by amines

The reactions of different halogen-containing polymers with amines have been widely studied and reported in the literature. A number of studies describe the dehydrohalogenation of PVC,[68–74] PVDC,[75,76] and their copolymers,[77] poly(vinyl bromide),[78] poly(α-chloroacrylonitrile),[79,80] as well as a number of fluorine-containing polymers[81,82] by aliphatic primary,[68,77,81] secondary,[68,75,81] and tertiary[68,74,78–81] amines, a wide range of aromatic amines such as aniline and its derivatives,[69,70,77,81] and also pyridine.[71–73,76,78,81]

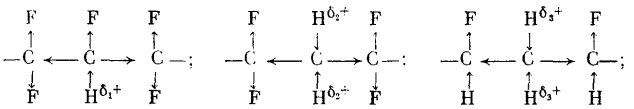
On reacting halogen-containing polymers with amines two competing processes occur—dehydrohalogenation and amination.[68–70,77,81,82] As the basicity of the amines used increases, the proportion of dehydrohalogenation reactions increases.[68,69,71,81] Amination can occur through the replacement of a halogen atom in the polymer chain[68,69,77] or addition to the double bonds formed by dehydrohalogenation.[81,82] Depending on the reaction conditions, the amination products can undergo intramolecular cyclisation[69,70] and intermolecular cross-linking.[68,69,77,82] Degradation of the macromolecules through the formation of carbocations[69] and aminolysis[81] is also possible. It should be noted that as the concentration of amine increases the proportion of amination reactions increases.[69]

Reactions between halogen-containing polymers and amines have been carried out over a wide temperature range—from room temperature to 200 °C. Aliphatic amines react with halogen-containing polymers even at room temperature[68,77] whereas a considerable increase in temperature is required for aromatic amines.[69,77]

The reactivity of halogen-containing polymers in dehydrohalogenation reactions increases with an increase in the number of halogen atoms in the fundamental unit. Thus, on treatment with n-butylamine at 78 °C, films made of poly(vinyl fluoride) $-(CH_2-CHF)_n-$ were inert towards the amine for 24 h. Films made of PVDF $-(-CH_2-CF_2-)-$ become black and brittle over a period of 4 h while for films made of polytrifluoroethylene $-(CHF-CF_2-)_n-$ this occurred over a period of 10 min.[81] Thus, these polymers can be arranged in the following order of reactivity:

$$-(-CHF-CF_2-)_n- > -(-CH_2-CF_2-)_n- > -(-CH_2-CHF-)_n-.$$

This effect is due to the fluorine (halogen) atoms having strong electron-withdrawing properties. As a result of the shift in electron density from the carbon atoms to the fluorine atoms, which in turn is compensated by a shift in electron density from the hydrogen atoms to the carbon atoms, the electrophilicity of the hydrogen atoms increases, thus assisting the removal of a proton by a base.[81] Thus, the reduction in reactivity in this series of fluoropolymers is caused by the reduction in electrophilicity of the hydrogen atoms:

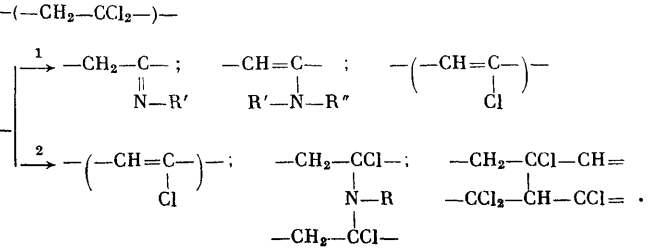


$\delta_1^+ > \delta_2^+ > \delta_3^+$.

In the IR spectra of the reaction products there are absorption bands which are characteristic of stretching vibrations of conjugated C=C double bonds (in the region of 1600 cm^{-1})[68,69,77,79] as well as N–H bonds (at about 3400 cm^{-1}).[68,69]

An analysis of the UV and visible absorption spectra of the products of the reaction between vinylidene chloride–vinyl chloride copolymer and various amines in comparsion with the spectra of β-carotene has been carried out.[77] In the spectrum of β-carotene characteristic absorption bands occur at wavelengths of 435, 460, and 486 mμ, whereas in the spectra of the products of the reaction between the copolymer and amines, no specific absorption bands were detected. On the basis of this observation, Nakagawa[77] concluded that the chromophoric groups of the reaction products differ considerably from the corresponding group in β-carotene with quite a long chain (11 units) of conjugated C=C bonds, i.e., the sections of conjugation in the dehydrochlorination products of the vinylidene chloride–vinyl chloride copolymer are shorter in length. Nakagawa attributes this to the fact that this copolymer has the structure of a block copolymer and therefore propagation of the chain of conjugation during dehydrochlorination, which is initiated on the more reactive vinylidene chloride units, is terminated on the vinyl chloride units.[77] It should be noted that amination and cross-linking reactions can also be the cause of breaks in the chain of conjugation. With an increase in basicity of the amines used, the rate of reaction increases and the proportion of dehydrohalogenation reactions increases. Thus, in dehydrochlorination of the above-mentioned copolymer, the amines used were arranged in the following order of reactivity: n-butylamines > cyclohexylamine ≫ N-methylaniline > aniline > *N,N*-dimethylaniline.

Depending on the basicity of the amine, reactions that occur with halogen-containing polymers can be divided into two types in accordance with the following scheme (in the case of PVDC);[77]

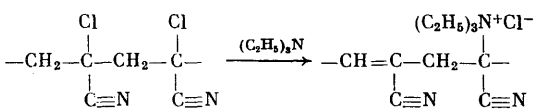


When an amine with low basicity (pK_a = 4–5) is used, the reaction takes place by scheme (*1*). In this case amination reactions occur to a considerable extent by a nucleophilic substitution mechanism (R′ = phenyl, R″ = methyl). When an amine with high

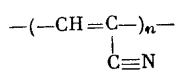
basicity is used (pK_a = 9–10) the reaction occurs by scheme (*2*). In this case dehydrochlorination is predominant at the initial stages of the reaction, while amination can occur by a mechanism involving the addition of amines (R = n-butyl, cyclohexyl) to the double bonds that are formed.[77]

Dehydrochlorination of poly(α-chloroacrylonitrile) (PCAN) in acetone solution by triethylamine results in the formation of a black polymer which is soluble in polar solvents and even in water.[79,80] In the IR spectra of the reaction products the absorption bands characteristic of C–Cl bond vibrations (640 cm^{-1}) in the initial polymer have disappeared and strong absorption bands at 1640 and 1730 cm^{-1}, characteristic of vibrations due to conjugated C=C bonds and O=C< carbonyl groups respectively, have appeared. In the region of 2100–2200 cm^{-1} appear two strong absorption bands that are characteristic of vibrations due to nitrile groups N≡C– that are conjugated (2215 cm^{-1}) and isolated (2250 cm^{-1}) relative to the main chain.[80]

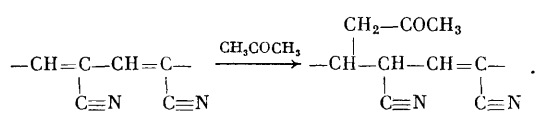
The solubility of the dehydrochlorination product of PCAN is caused by side reactions involving replacement of the chlorine atoms by a tertiary amine to form quaternary ammonium substituents



In fact, when the dehydrochlorination is heated for 4–5 h under vacuum at 180–190 °C triethylamine hydrochloride sublimes. At the same time there is a loss of solubility in water. In the IR spectrum of the thermally treated dehydrochlorination product the absorption band at 2250 cm^{-1} (isolated N≡C– groups) disappears and the strong band at 2200 cm^{-1} (conjugated N≡C– groups) remains. A very broad absorption band occurs over the range 1000 to 1700 cm^{-1} with a peak at 1630 cm^{-1}, which is characteristic of stretching vibrations due to conjugated C=C bonds of the polymer chain. Its complete solubility in DMF excludes the formation of cross-linked structures, so the final product of dehydrochlorination and thermal treatment of PCAN is assigned the polycyanopolyene (polycyanoacetylene) structure[80]

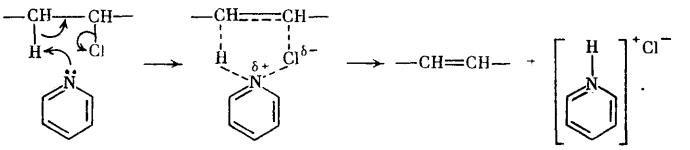


The presence of carbonyl groups in the dehydrochlorination products of PCAN is due to the occurrence of side reactions involving the addition of acetone to C=C double bonds, which is assisted by the strong electron-withdrawing effect of N≡C– groups:

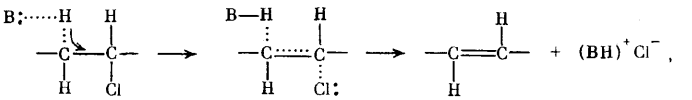


Reversible alkoxylation on the C=C double bonds takes place in a similar manner when dehydrochlorination is carried out with alkali metal alkoxides.[80]

In the reaction between halogen-containing polymers and pyridine at elevated temperatures dehydrohalogenation mainly occurs.[71–73,76] Poly(vinyl chloride) and pyridine have different solubility parameters (9.4 and 10.7 respectively), but PVC readily dissolves in pyridine. This is possible only if there is a specific interaction between pyridine and PVC. Therefore, by analogy with the mechanism for dehydrochlorination of PVC in dimethylformamide,[84,85] a mechanism for dehydrochlorination was proposed which included the formation of an intermediate complex between pyridine and polymer, assisting the elimination of HCl in the form of pyridine hydrochloride:[71,72]



Subsequently, on the basis that the double bonds formed by dehydrohalogenation mainly have a *trans* configuration, the reaction mechanism scheme was refined in the following way:[73]



B = pyridine.

With an increase in reaction temperature and time the degree of dehydrochlorination increases steadily.[71] The length of the polyene sequences and the total number of double bonds in the reaction products also increase steadily with an increase in time of dehydrochlorination.[72]

At the advanced stages of dehydrochlorination the polymer is precipitated from the reaction solution, which Mukherjee and Gupta[71,72] assume to be due to intensive cross-linking. It should be noted, however, that with an increase in the length of conjugation in the chain, the solubility of the reaction products decreases, which can also be the cause of precipitation of the polymer from solution.

At high temperatures and a prolonged reaction time the dehydrochlorination and cross-linking processes compete. The authors proposed a scheme involving intermolecular dehydrochlorination for the cross-linking reaction.[72] However, taking into account the mechanism for dehydrohalogenation as described above, involving β-elimination in the polymer chain, it may be concluded that the probability of an interchain dehydrohalogenation occurring is much less than an intrachain one. It is more probable that cross-linking processes occur by the mechanisms proposed for polymers with a system of conjugated multiple bonds, for example, that of polyacetylene.[86]

It should be noted that in the IR spectra of the products of dehydrochlorination of PVDC by amines, absorption bands corresponding to the vibrations of triple (–C≡C–) or cumulated (=C=C=) carbon–carbon double bonds were absent.[75–77]

V. Dehydrohalogenation by dimethylformamide

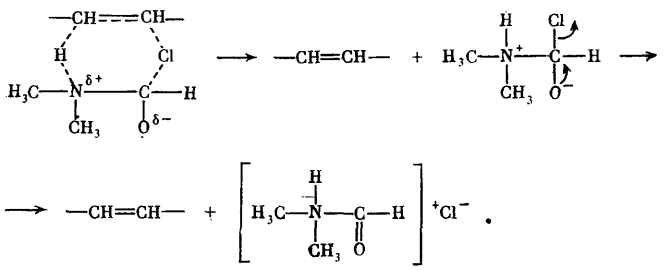
Certain *N*-substituted amides, such as *N*-methylpyrrolidone, *N,N*-dimethylacetamide (DMAA), and *N,N*-dimethylformamide (DMF), are polar aprotic solvents that have basic properties. Even with a slight increase in temperature they can eliminate HCl from PVC to form polyene structures.[83] The dehydrochlorination of PVC in DMF solution has been studied in the greatest detail in this field.[83–85,87–92]

In a study of the degradation of PVC in solution at a high temperature (198 °C) it was found that the rate of dehydrochlorination in DMF was higher than the rate of reaction in other high-boiling solvents such as ethyl benzoate, tritoluyl phosphate, dibutyl phthalate, dioctyl phthalate, benzophenone, benzyl alcohol, and dichloronaphthalene by a factor of more than 10^2.[84,87]

Moreover, according to the UV spectroscopic data, the length of the polyenes formed when the reaction was carried out in DMF considerably exceeded the length of the chain of conjugation when the above-mentioned high-boiling solvents were used.[85,87]

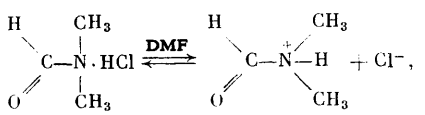
This effect is due to an interaction between PVC and DMF. This conclusion is supported by the fact that PVC is readily soluble in DMF despite the considerable difference in solubility parameters (9.6 and 12.1 respectively).[85] The role of the amide in dehydrochlorination was supported experimentally when the degradation of PVC was carried out in ethyl benzoate in the presence of acrylamide.[84]

As a result of the formation of an intermediate complex between DMF molecules and the fundamental units of the polymer, the dissociation energy of the C–H and C–Cl bonds is reduced, assisting the elimination of HCl.[84,85,87] The HCl separated by dehydrochlorination binds to the solvent:

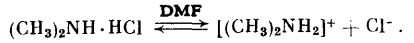


The dehydrochlorination of PVC in DMF is autocatalytic in nature. This is due not only to the action of DMF [88] but also to the effect of amine-type impurities[89,90] present in it as well as the reaction products (HCl and Cl^-) accumulating in solution.[90] Dimethylformamide, even when freshly prepared, always contains small quantities of dimethylamine, formic acid, and dimethylammonium formate,[93] the content of which varies from 10^{-3} to 10^{-2} mol litre^{-1}.[90] Moreover, at high temperatures DMF decomposes to dimethylamine and formic acid. The destruction of DMF can be accelerated by the HCl eliminated during dehydrochlorination.[94] Dimethylformamide hydrochloride,[95] formed during dehydochlorination, decomposes at temperatures above 90 °C to carbon monoxide and dimethylamine hydrochloride, which can also catalyse dehydrochlorination.[85] The rate of dehydrochlorination of PVC in dilute DMF solutions is directly proportional to the concentration of free dimethylamine. By extrapolation of the rate of reaction to zero concentration of dimethylamine, it is possible to estimate the dehydrochlorination of PVC in "absolutely pure" DMF. The rate of reaction in pure DMF is 10^2 times higher than the rate of degradation of PVC powder in the absence of a solvent with other conditions being equal.[90]

The dimethylformamide and dimethylamine hydrochlorides formed during dehydrochlorination in DMF solution are present in a dissociated state[96]



or



Halide ions in dipolar aprotic solvents (such as DMF, DMAA, etc.) are both strong bases and strong nucleophiles[97] and can accelerate dehydrochlorination.[90]

Thus, the autocatalytic nature of the dehydrochlorination of PVC in DMF is due to the effect of amine-type impurities and the reaction products (HCl and Cl^-).

A kinetic equation for the autocatalytic dehydrochlorination of PVC in DMF solution which is in good agreement with the experimental data was derived empirically[88]

$$dX/dt = kX\cdot(1 - X),$$

where X is the number of moles of eliminated HCl per fundamental unit of HCl, k is the rate constant of the reaction. However, it was shown subsequently[91] that this equation is approximate and can only be used to represent the kinetics of dehydrochlorination of PVC in DMF at a high concentration of polymer and high reaction temperatures. At the initial stage, dehydrochlorination is initiated in a basic medium (pH 10–12) and results from the interaction between PVC and DMF and amine-type impurities. As HCl is eliminated the pH of solution is reduced to 4–2 and Cl^- and HCl become the main catalytic agents. Therefore, to represent the kinetics of the process Fikhman et al.[91] used an equation with two rate constants, proposed for the autocatalytic thermal degradation of PVC powder

$$q = \frac{K_1}{K_2}\left\{\exp\left[K_2\left(1+\frac{K_1}{K_2}\right)t\right]-1\right\}\Big/\left\{1+\frac{K_1}{K_2}\exp\left[K_2\left(1+\frac{K_1}{K_2}\right)t\right]\right\},$$

where q is the quantity of HCl eliminated from PVC after time t per fundamental unit of polymer; K_1 is the rate constant of dehydrochlorination of PVC due to the basicity of DMF; K_2 is the overall rate constant, including the catalytic effect of chlorine-containing products formed in solution.[92] This equation effectively represents the experimental results obtained in the dehydrochlorination of PVC in DMF over a wide range of temperatures, concentrations of polymer, and different added components used to inhibit or accelerate dehydrochlorination.[91]

In general the dehydrochlorination of PVC in DMF solution should be given by an S-shaped curve, which can arbitrarily be divided into three sections: 1) acceleration of dehydrochlorination catalysed by DMF and basic impurities; 2) the autocatalytic action of HCl and the Cl^- ion is superimposed on it in an acid medium; 3) dehydrochlorination is inhibited by cross-linking of dissolved PVC and the formation of long conjugated polyenes.[91] The first two sections are effectively represented by the kinetic equation with two constants. The energies of activation of dehydrochlorination calculated from the Arrhenius equation in two different studies[91,88] are similar (23.5 ± 0.5 and 22.2 kcal mol^{-1} respectively).

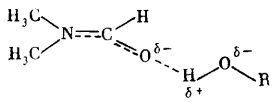
When dehydrochlorination was carried out under vacuum or in an atmosphere of nitrogen the length of the resulting conjugated polyenes amounted to 13–16 –CH=CH– units, whereas in the presence of oxygen it did not exceed 4–5 units, which is due to oxidation of the double bonds, leading to breaks in the chain of conjugation.[85]

On increasing the concentration of polymer in solution, the length of the resulting polyenes increases. As the reaction progresses dehydrochlorination slows down, which is due to partial cross-linking of the polymer as a result of side reactions and a reduction in activity of the macromolecular segments as well as the formation of polyenes with a long chain of conjugation.[91]

The degree of dehydrochlorination increases with an increase in reaction time. When THF is added to the reaction solution, the rate of reaction and degree of dehydrochlorination decrease in direct proportion to the concentration of DMF. On increasing the

concentration of polymer in solution the rate of reaction and degree of dehydrochlorination increase.[98]

Addition of water or methanol to the reaction solution results in considerable inhibition of dehydrochlorination, which is due to the formation of hydrogen bonds and hence a reduction in basicity of DMF:[98]



R = H or CH_3.

A study of the reaction of PVC in different solvents at temperatures of 100–170 °C showed that in solvents that have considerable nucleophilicity and basicity (pyridine, morpholine) dehydrochlorination and substitution reactions occur in parallel. In solvents that have considerable basicity but weak nucleophilicity (DMF, DMAA), elimination of hydrogen halide mainly occurs. In solvents that have weak nucleophilicity and basicity (THF, cyclohexanone, nitrobenzene), PVC remained unchanged. When solvents that have weak basicity but strong nucleophilicity are used (dioctyl phthalate, benzyl alcohol), substitution reactions occur to a considerable degree.[98]

VI. Dehydrohalogenation by complexes of *N*-substituted amides with metal salts

In a number of studies the dehydrohalogenation of PVC,[99–104,106,107,109–111] poly(vinyl bromide),[99] and also PVDC, CPVC, and vinylidene chloride–vinyl chloride copolymer[111] by complexes of *N*-substituted amides with metal salts has been investigated.

The structure of the dehydrohalogenation products depends on the reaction conditions, the structure of the initial polymer, and also on the nature of the solvent (amide) and salt used.

On increasing the content of the metal salts in solution, the concentration of polymer, and the reaction temperature (from 80 to 110 °C), the degree of dehydrohalogenation and the rate of reaction increase.[99–101] The degree of dehydrohalogenation also increases with an increase in reaction time[99,100] and the degree of polymerisation of the initial polymer.[102]

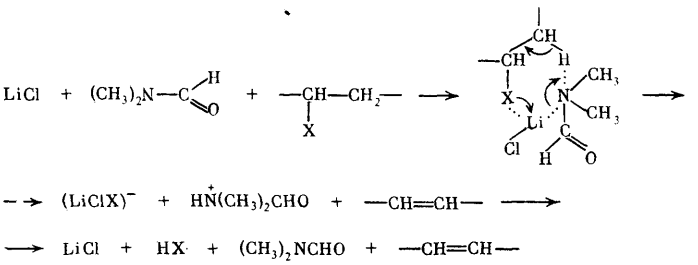
The presence of oxygen in the reaction mixture leads to a reduction in the rate of dehydrohalogenation and to the occurrence of side reactions involving degradation of the polymer.[102] Dilution of the reaction solution with tetrahydrofuran leads to a reduction in the degree of dehydrohalogenation and the rate of reaction.[99]

It should be noted that on reaching a degree of conversion of 30–40% the dehydrohalogenation products become insoluble and precipitate from solution.[99]

As dehydrochlorination of PVC takes place, in the IR spectra of the reaction products there is a decrease in intensity of the absorption band in the region of 690 cm^{-1} which is a characteristic of stretching vibrations due to C–Cl bonds in the initial polymer and new intense absorption bands appear in the region of 1000 and 1600 cm^{-1} that are characteristic of C–H bond bending vibrations in *trans*-polyenes and stretching vibrations due to conjugated C=C double bonds respectively.[101,103,104] A very weak band appears in the region of 730 cm^{-1} which could be attributed to bending vibrations of the C–H bonds on a C=C double bond in a *cis* configuration.[104] When dehydrochlorination is carried out in the presence of oxygen, an intense absorption band occurs in the IR spectra of the products at 1760 cm^{-1} which is characteristic of vibrations due to the O=C< group.[103]

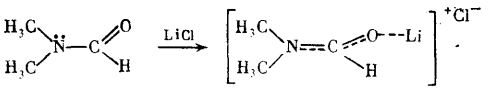
Dehydrochlorination of PVC in the system DMF–LiCl ($LiBr_2$, $MgCl_2$) resulted in the formation of long polyene structures with the number of conjugated double bonds $n > 14$. A broad maximum occurred at 550 mμ in the absorption spectrum in the UV and visible regions. In the spectra of the dehydrochlorination products of PVC in the system DMF–lithium acetate or magnesium chloride hydrate ($MgCl_2 \cdot 6H_2O$) a series of maxima that are characteristic of absorptions due to relatively short polyenes with the number of units $n = 4-14$ is observed. Zinc, copper, cobalt, nickel, and cadmium chlorides as well as lithium carbonate proved inactive in dehydrohalogenation.[99]

The system LiCl–DMF was first used in the dehydrobromination of bromoketosteroids,[105] and a mechanism for this was proposed that involved elimination of hydrogen halide as a result of the simultaneous attack by a lithium cation and DMF on alkyl halide and the concerted electron rearrangement in a six-membered ring including the halogen-containing compound, a DMF molecule, and a LiCl molecule:



X = halogen.

However, this mechanism, in attaching most importance to the coordinating power of the cation, does not explain the activity of some salts and the inactivity of others in dehydrohalogenation.



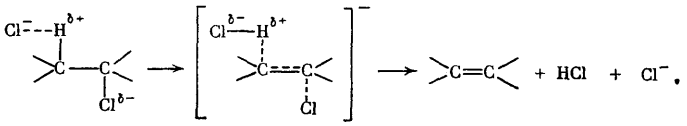
Lithium chloride forms a stable complex with DMF,[101] which occurs in dissociated form in DMF solution. As was mentioned above in Section V, halide ions in dipolar aprotic solvents are strong bases and nucleophiles.[97] Therefore the main dehdyrohalogenating agents in the sytstem DMF–metal salts are anions (in particular Cl^-)[99] and their ion pairs.[106,107] Nucleophilic substitution of halogen atoms in polymers by Cl^- and Br^- atoms does not inhibit further dehydrohalogenation. But if irreversible substitution reactions with nonhalide ions occur, the length of the polyene sequences formed during reaction is limited by the presence of these substituents. Thus, when lithium acetate or magnesium chloride hydrate is used for dehydrohalogenation, substitution reactions by the acetate and hydroxyl groups lead to a decrease in length of the resulting polyenes.[99]

Despite their solubility in DMF, heavy metal salts do not dissociate,[108] which accounts for the inactivity of these salts in dehydrohalogenation. Moreover, some salts form stable complexes with DMF (such as $ZnCl_2$) and inhibit dehydrohalogenation.[90,102]

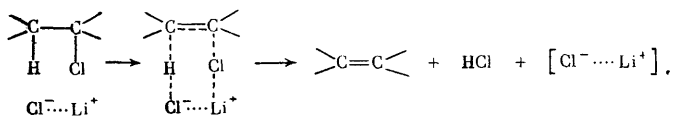
The rate of dehydrochlorination of PVC in the presence of LiCl and the structure of the reaction products depend to a considerable extent on the stereostructure (tacticity) of the initial polymer and the

polarity of the solvent.[102,106,109] When hexamethyltriamidophosphate (HMTP) is used as the solvent, the rate of reaction and length of the resulting polyenes are considerably greater than that when DMF is used.[106,109] Dehydrochlorination of syndiotactic PVC in both DMF and HMTP results in the formation of considerably longer polyene structures than with an atactic polymer. On increasing the syndiotactic content in the initial PVC, the rate of dehydrochlorination in DMF decreases (the energy of activation increases sharply), whereas in HMTP the rate of reaction increases and the energy of activation decreases.[106,109] This phenomenon is attributed to the existence of two parallel dehydrohalogenation mechanisms that are in an equilibrium which is shifted in favour of one of them depending on the stereostructure of the initial polymer and the polarity of the solvent.[106]

(A). Mechanism involving β-elimination $(E_2)^1$ by a halide ion (Cl^-):



(B). Mechanism involving dehydrohalogenation by a $[Cl^- \ldots Li^+]$ ion pair:



If the role of the solvent is ignored, it may be observed that a syndiotactic structure of the polymer is conducive to mechanism (A)' whereas an isotactic structure assists mechanism (B).

The concentration of unsolvated Cl^- anion and solvated Li^+ ion is considerably higher in HMTP than in DMF. Therefore the basic nature of Cl^- is more clearly defined in HMTP and hence, ionic mechanism (A) predominates in the dehydrochlorination of PVC, whereas in DMF mechanism (B), involving the action of an ion pair, is predominant.[106]

The energy of activation of dehydrochlorination in each specific case is the sum of the energies of activation of the respective mechanisms and depends on the tacticity of the initial polymer and the polarity of the solvent. The length of the polyene chains thus depends not only on the contribution from side reactions involving cross-linking, substitution, and oxidation but also on the equilibrium between the dehydrohalogenation mechanisms. Ionic elimination (A) leads to the formation of longer polyenes than with the ion-pair mechanism (B).[106]

On the whole, dehydrochlorination of PVC in the system DMF–LiCl involves two stages. At the first (rapid) stage dehydrochlorination of iso- and hetero-tactic structures in the macromolecules takes place with the formation of short polyene residues. At the second (slow) stage dehydrochlorination of the syndiotactic structures occurs with the formation of long sequences of conjugated C=C double bonds.[110] The variation in length of the polyenes formed during dehydrochlorination depending on the tacticity of the initial PVC is due to the stereospecific nature of the fundamental stages of elimination of HCl.[104,110]

The activity of the alkali metal salts depends on the electronegativity of the cation and the dipole moment of the salt. The rate of dehydrochlorination of PVC increases in the series LiI < NaI < KI < RbI. The solvating capacity of DMF relative to the cation of the ion pair $M^+(DMF)_nI^-$ (M = metal) increases as the electronegativity of the cation decreases (from 1.0 for Li to 0.8 for Rb). Therefore, as the electronegativity of the M^+ cation decreases, the contribution from the solvent increases and the anion of the ion pair approximates in nature to a free ion, in other words, its basicity increases.[107]

In a series of lithium halides the rate of dehydrochlorination increases in the following order: LiI < LiBr < LiCl.[107] Solvation of anions decreases as their diameter decreases,[97] hence the basicity of the anions in solution increases.

The use of lithium salts formed by anions having significant nucleophilicity (cyanide, thiocyanate, nitrite, as well as organic salts such as acetate, benzoate, phenate, and thiophenate) led to a reduction in the rate of dehydrochlorination compared to the system LiCl–DMF and the formation of short polyenes as a result of side reactions involving substitution.[101]

The rate of dehydrochlorination of PVC by the system LiCl–DMF is given by the equation[101]

$$dHCl/dt = k_1.[PVC].[LiCl] + k_2.[PVC]_1.[LiCl] + \ldots + k_n.[PVC]_{n-1}.[LiCl],$$

or

$$dHCl/dt = k_1.[PVC]_0.[LiCl].e^{-k.[LiCl].t},$$

where k_n is the rate constant of a simple elimination to form 1, 2, ... n conjugated double bonds; $[PVC]_0$ is the initial concentration of PVC; $[PVC]_n$ is the concentration of macromolecules containing 1, 2, ... n conjugated double bonds; [LiCl] is the concentration of LiCl; and t is the reaction time.

For the initial rate of reaction (when $t \to 0$) the kinetic equation has the form

$$dHCl/dt = k_1.n.[PVC]_0.[LiCl].$$

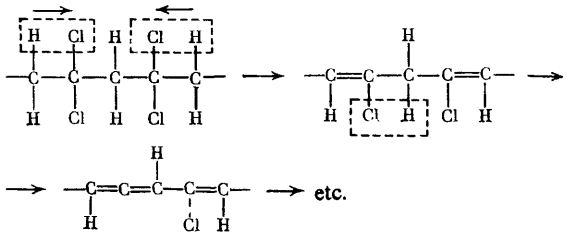
Dehydrochlorination of polymers containing more than one chlorine atom per monomer unit (PVDC, CPVC, and vinylidene chloride–vinyl chloride copolymer) occurs much more rapidly compared to pure PVC and reaches higher degrees of conversion (in the dehydrochlorination of PVDC about 1.4 chlorine atoms are eliminated on average per monomer unit).[111] This effect is consistent with the results obtained in a study of the dehydrofluorination of fluorine-containing polymers by amines[81] and is due to the increase in activity of the hydrogen atoms and a reduction in the dissociation energy of the carbon–halogen bond as the content of halogen in the polymer increases.

The structure of the reaction products during dehydrochlorination by the system LiCl–DMF also depends on the content of chlorine in the initial polymers. In the dehydrochlorination of polymers containing up to 64% chlorine, long polyene sequences are formed with the number of conjugated double bonds $n > 14$. However, dehydrochlorination of polymers containing more than 64% chlorine leads to the formation of relatively short polyenes ($n = 6-13$).[111] Laurent et al.[111] attribute this phenomenon to the "mutual restriction" of the growing polyene residues through their isolation by a methylene carbon atom:

$$-CH=CH-CH=CH-CH_2-CH=CH-CH=CH-.$$

With an increase in chlorine content in the polymer the rate of initiation of dehydrochlorination increases and therefore several growing polyene sequences can be formed at the same time in the polymer chain, which increases the probability of their "mutual restriction". However, this explanation of the interrruption of conjugation is acceptable only for PVC and poly(vinyl bromide).

Taking into account the degree of dehydrochlorination reached, where in the case of PVDC 1.4 Cl atoms are eliminated on average per monomer unit, it may be concluded that for polymers with a high chlorine content, the methylene and chloromethylene groups remaining in the polymer as a result of the "mutual restriction" of the growing polymers should undergo further dehydrochlorination:



The decrease in length of the resulting polyenes with an increase in chlorine content in the initial polymers is likely to be due to side reactions involving cross-linking at a relatively high temperature of dehydrochlorination (80–100 °C). Moreover, according to elemental analysis and IR spectroscopic data, the reaction products contain nitrogen- and oxygen-containing groups, which the authors assign respectively to free DMF retained by the precipitated polymer or to oxidised structures. However, it is possible that with an increase in the chlorine content of the polymer, the probability of substitution reactions taking place between the halogen-containing polymer and DMF or its degradation products is increased.

VII. Dehydrohalogenation by alkali metal amides

In a number of studies dehydrochlorination of PVC,[112–115] CPVC,[113,114] and PVDC [113,114,116–118] by alkali metal amides in liquid ammonia was investigated. The reaction has been carried out over a wide temperature range (from −60 to 50 °C) with polymer solutions and also powders and films. When dehydrohalogenation is carried out at temperatures above −33 °C (the boiling point of ammonia) an increase in pressure in the reactor is required.

By using alkali metal amides it is possible to achieve complete dehydrohalogenation even at low temperatures, which reduces the contribution from side reactions involving cross-linking to a minimum and assists the formation of structures with long sequences of conjugated multiple bonds. Thus, for example, completely dehydrochlorinated PVC, which contains no chlorine, melts at a temperature of 395–410 °C,[112,115] which is an indication of the linear structure of the dehydrochlorination product (absence of spatial cross-linking).

Dehydrohalogenation of halogen-containing polymers in solution[114] occurs more rapidly than with powders or films.[45] The degree of dehydrohalogenation increases with an increase in temperature and reaction time as well as with an increase in concentration of the alkali metal amide.[113,114,117]

As dehydrochlorination takes place the absorption bands characteristic of the initial polymers in the IR spectra of the products disappear and absorption bands appear at 990, 1600, and 3030 cm^{-1}, characteristic of bending vibrations of C–H bonds on a *trans*-C=C double bond, stretching vibrations of conjugated C=C double bonds, and stretching vibrations of the C–H bonds on a C=C double bond respectively.[45,113–117] In the IR spectra of the dehydrochlorination products of PVDC and CPVC an absorption band also occurs at 2200 cm^{-1}, which is attributed to stretching vibrations of C≡C triple bonds.[45,113,114,116,117]

A study of the dehydrochlorination products of PVC using X-ray diffractometry showed that these products have a structure that is similar to that of noncrystalline *trans*-polyacetylene.[114,115]

In the EPR spectra of the products of the complete dehydrochlorination of PVC a narrow solitary signal appears with a line width of 7–12 E.[112,114,115] As the degree of dehydrochlorination increases the line width decreases.[115] The value of the *g*-factor is 2.000 ± 0.005.[112] For the dehydrochlorination products of PVDC a narrower line in the EPR spectrum (5–9 E) is characteristic. As the degree of dehydrochlorination increases the spin-lattice relaxation time decreases and reaches a value of 10^{-6} s.[116]

From an examination of the EPR spectra it may be concluded that delocalisation of the unpaired electrons, which are stabilised by the long chain of conjugated multiple bonds, occurs in the dehydrochlorination products.[114] As the degree of conversion increases, the concentration of unpaired electrons increases and reaches a value of 1.4×10^{21} spin g^{-1} for the dehydrochlorination product of PVDC.[116]

It should be noted that dehydrochlorination of PVDC by alkali metal amides in liquid ammonia has been proposed as a counter-synthesis of carbyne[116] occurring by a two-stage mechanism[117]

$$-(-CH_2-CCl_2-)_n- \xrightarrow[-n\,HCl]{} -(-CH=CCl-)_n- \xrightarrow[-n\,HCl]{}$$

$$\longrightarrow -(-C\equiv C-)_n-$$

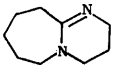
In four studies[112–115] elemental analysis data are given according to which the sum of the content of carbon and hydrogen in products of the exhaustive dehydrochlorination of PVC, containing no chlorine, differs from 100%. The authors attribute this difference to the presence of oxygen that is formed in the dehydrochlorination products as a result of oxidation reactions. Moreover, completely dehydrochlorinated PVC and PVDC did not contain nitrogen.[112–115] However, in a study[117] of the dehydrochlorination of PVDC with sodium and potassium amides in liquid ammonia at −55 and 0 °C it was shown that the main process of HCl elimination is accompanied by amination as a side reaction. Thus, for example, when dehydrochlorination was carried out at 0 °C for 30 h, the reaction products contained 8.3% nitrogen. It was shown that the content of nitrogen in the reaction products rises with an increase in the time of dehydrochlorination, the concentration of alkali metal amide in solution, and the degree of dehydrochlorination.[117]

In fact, alkali metal amides have considerable nucleophilicity in addition to high basicity. Therefore, when the dehydrohalogenation of halogen-containing polymers by alkali metal amides in liquid ammonia is carried out, side reactions involving nucleophilic substitution of the halogen atoms are to be expected. In addition to this, addition reactions of ammonia to multiple bonds are also possible[117]

$$-(-C\equiv C-)- \xrightarrow[NH_3]{NH_2^-} -\underset{\underset{H}{|}}{\overset{H}{\overset{|}{C}}}-\underset{\underset{NH}{\|}}{\overset{|}{C}}-C\equiv C-.$$

VIII. Dehydrohalogenation by 1,8-diazabicyclo-[5.4.0]undec-7-ene

In recent years studies in which the strong organic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)



is used as a dehydrohalogenating agent for halogen-containing polymers have made their appearance in the scientific literature.[58,119–122]

Soga et al.[58,119] studied the dehydrochlorination of samples of PVC with a varying degree of polymerisation by DBU in polar solvents. The solvents used were dimethyl sulphoxide, THF, HMTP, and DMF. The reaction was carried out at 65 °C for 20 h. It was shown that the degree of dehydrochlorination did not depend on the molecular weight of the initial PVC.

As a result of dehydrochlorination long sequences of conjugated C=C double bonds are formed. A determination of the length of the polyene sequences from the data of elemental analysis gave a value of 8–15 –CH=CH– units. Samples of dehydrochlorinated PVC contained 2.8–4.9% residual chlorine and also 5.0–7.5% nitrogen, which in the opinion of the authors, was due to the partial doping of the resulting polyene with DBU molecules.[58]

In the IR spectra of the dehydrochlorination products a very strong absorption band occurs at 1015 cm^{-1} which is characteristic of a *trans*-polyacetylene.[58,119] In the UV spectra a broad absorption band occurs in the region of 670 nm, which is attributed to $\pi \rightarrow \pi^*$ electronic excitations.[58] After partial hydrogenation of the dehydrochlorination product of PVC alloyed with potassium, absorption bands occurred at 240, 280, 310, 340, 380, 400, and 420 nm in the UV spectra, which were attributed by the authors to $\pi \rightarrow \pi^*$ transitions in $-(-CH=CH-)_n-$ structures, where n = 2, 3, 4, 5, 6, 7, and 8 respectively.[119]

In the X-ray diffraction spectrum of the polyenes obtained there is a weak halo at 2θ = 20–25 °C, which is an indication of the very low degree of crystallinity.[58] With an increase in molecular weight of the initial PVC the intensity of this halo decreases, which suggests a decrease in the degree of crystallinity.

The dehydrochlorination of PVC films was studied by Danno et al.[120,121] Dehydrochlorination was carried out in two stages. At the first stage the reaction was carried out in a mixture of DMF and methanol at a volume ratio of 2:3 at 50 °C for 36 h in a current of nitrogen, in order to prevent the PVC films dissolving in the reaction mixture. As dehydrochlorination took place, in the IR spectra of the reaction products the intensity of the absorption bands due to C–Cl bonds in the region of 600–700 cm^{-1} that were characteristic of the initial PVC decreased and new bands appeared at 1010 and 3015 cm^{-1}, characteristic respectively of bending and stretching vibrations of C–H bonds in *trans*-polyacetylene.

The degree of dehydrochlorination increases with an increase in concentration of DBU and also with an increase in reaction time up to 40 h, reaching a value of 0.8 and then remaining constant (at a molar ratio of DBU:Cl = 4:1).[120]

A well-defined absorption band occurs at 605 cm^{-1} in the IR spectra of the films after the first stage of dehydrochlorination. This band is absent in the spectra of the initial PVC, whereas a band is clearly defined at 615 cm^{-1}. The absorption bands in the IR spectra at 605 and 615 cm^{-1} are attributed to stretching vibrations of C–Cl bonds in crystalline and amorphous PVC respectively. Thus, during dehydrochlorination at the first stage, elimination of HCl mainly occurs in the amorphous phase of PVC whereas the crystalline region does not change. Therefore, the maximum degree of dehydrochlorination attained at the first stage (0.8) is due to the presence in the initial PVC of about 20% as a crystalline fraction, which is more resistant to dehydrochlorination.[120]

After the first stage of the reaction the films became insoluble, which made it possible to use pure solvents at the second stage. For this second stage the reaction was carried out in pure DMF at 50 °C for 24 h in a current of nitrogen. The authors anticipated that at the second stage the crystalline regions of PVC would swell in the solvent and undergo further dehydrochlorination. In fact, the degree of dehydrochlorination increases to 0.95 at the second stage. The absorption band at 605 cm^{-1} in the IR spectra of the reaction products almost completely disappears, which suggests that the crystalline fraction undergoes dehydrochlorination. In the spectra of the products, absorption bands occur at 1665, 1720, and 3450 cm^{-1}. The bands at 1665 and 1720 cm^{-1} are attributed to the absorption of α,β-unsaturated and isolated keto groups respectively. The band at 3450 cm^{-1} is attributed to the absorption of hydroxyl and hydroperoxide groups. The appearance of oxygen-containing groups in the reaction products is attributed by the authors to a reaction between polymer and DMF. When dehydrochlorination was carried out under similar conditions in cyclohexanone, methyl ethyl ketone, and THF, bands in the IR spectra corresponding to the absorption of oxygen-containing groups were absent or very weak.[120]

An increase in reaction time from 36 to 67 h at the first stage and from 24 to 48 h at the second stage did not produce any substantial changes in the degree of dehydrochlorination or the IR spectra of the products.[121]

A study of the dehydrochlorination products of industrial PVC using X-ray diffractometry showed that the resulting polyenes were completely amorphous,[120] whereas in the dehydrochlorination of syndiotactic PVC obtained by low-temperature polymerisation polycrystalline films of a similar polyene structure were obtained.[121]

The dehydrochlorination of stereospecifically chlorinated polyacetylene by DBU in different solvents was studied by Akagi et al.[122] In the IR spectra of the reaction products there are strong absorption bands in the region of 1640 and 2130 cm^{-1}, attributed to stretching vibrations of carbon–carbon double and triple bonds respectively. With an increase in polarity of the solvent used, the absorption band due to the triple bonds shifts from 2140 cm^{-1} (for toluene) to 2121 cm^{-1} (for dimethyl sulphoxide) and the degree of dehydrochlorination increases (from 80.8 to 100%). In the Raman spectra of the dehydrochlorination products, intense lines occurred in the region of 1550 and 1140 cm^{-1}, attributed to stretching vibrations of carbon–carbon double and single bonds respectively in conjugated *trans*-polyenes. The authors attribute the presence of these bands to incomplete chlorination of the initial polyacetylene. A line occurred at about 2150 cm^{-1} which was attributed by the authors to stretching vibrations of C≡C triple bonds in macromolecules of the polyyne modification of carbyne (α-carbyne). On increasing the wavelength of exciting light from 457.9 to 632.8 nm, the frequency of this line decreased from 2157 to 2113 cm^{-1} correspondingly. As a result of a numerical calculation from Raman spectroscopic data of the length n of the resulting polyynes using the empirical relationship

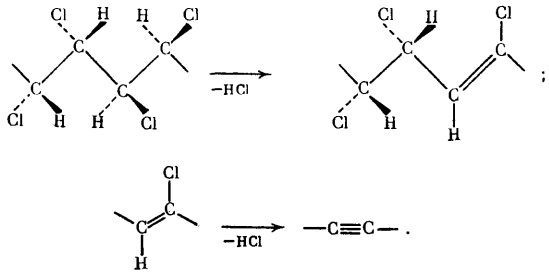
$$\nu_{C\equiv C} = 2104 + 698/(n_{C\equiv C} + 1)$$

values of n from 12 to 65 fundamental units were determined. Here $\nu_{C\equiv C}$ is the vibrational frequency of the C≡C bond in the Raman spectrum; n is the number of units of α-carbyne (–C≡C–).

In the UV spectra of the carbyne obtained there is a very broad absorption band from 350 to 700 cm^{-1}, which the authors attribute to overlap of the bands resulting from $\pi \rightarrow \pi^*$ excitations in the polyyne structures.[122]

The authors concluded from the IR and UV spectroscopic data that α-carbyne was formed and proposed a mechanism involving

two-stage *trans*-elimination:

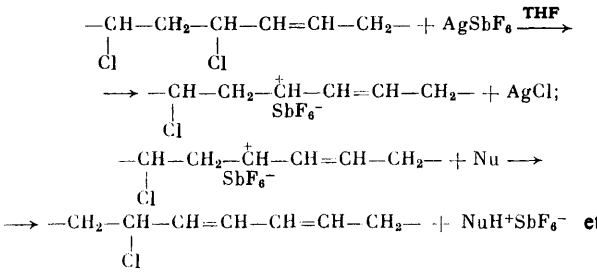


However, it should be noted that the results of vibrational spectroscopy alone are insufficient for an unequivocal conclusion about the type of bonding in the carbyne—polyyne or cumulene. Thus, according to calculated data which are good agreement with the experimental IR spectra, absorption bands in the region of 1600 and 2100–2200 cm^{-1} are characteristic of vibrations due to cumulene structures in β-carbyne molecules.[48] The absence of absorption bands at 1950 cm^{-1} in the IR spectra is not proof of the absence of a cumulene structure.[123,124] Moreover, assignment of the lines in the region of 1140 and 1550 cm^{-1} in the Raman spectra to vibrations of polyene structures[122] is only partly correct. Thus, while the line at 1140 cm^{-1} is due to the presence of polyacetylene residues in the sample, the intensity of the line in the region of 1550 cm^{-1} is disproportionately high for it to be assigned completely to vibrations of polyene structures.[125] The line in the region of 2150 cm^{-1} in the Raman spectrum was attributed by the authors to vibrations of the polyyne structures of α-carbyne. However, it was shown by Berdyugin et al.[54] that in the Raman spectra of β-carbyne obtained by dehydrohalogenation of poly(vinylidene halides) the lines in the region of 2150 and 1550 cm^{-1} correspond to vibrations of cumulated double bonds in the carbon chain. For a clear identification of the nature of the bonds in carbyne, a detailed study of its electronic structure is necessary.[33,41,42,51,52]

IX. Some other dehydrohalogenating agents

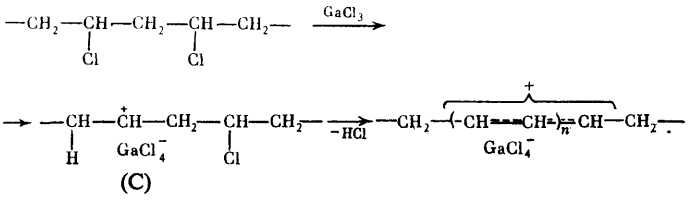
The chemical agents and systems that are widely used in the dehydrohalogenation of halogen-containing polymers are examined in Sections II–VIII. In the present section certain other chemical agents which are also active in hydrogen halide elimination reactions are described.

In the preparation of graft copolymers of isobutylene on PVC Kennedy and Davidson[126] found that organoaluminium compounds such as diethylaluminium chloride are able to dehydrochlorinate PVC to form a small quantity (2–5 mol%) of short $-(-CH=CH-)_n-$ polyene sequences, where $n \leqslant 5$ (according to UV spectroscopic data). In an attempt to obtain graft copolymers of THF on PVC it transpired that on treatment with silver hexafluoroantimonate dehydrochlorination of PVC occurred with the formation of polyene structures of 11 or more conjugated C=C double bonds,[127] while it was not possible to obtain graft copolymers. In the opinion of Kennedy[126] and Franta,[127] initiation of dehydrochlorination occurs at the sites of labile structures (mainly allylic chlorine atoms) present in the initial PVC. On replacement of the allylic chlorine atom by a SbF_6^- anion [or addition of a $(C_2H_5)_2AlCl$ molecule] a polymer carbocation is formed, which eliminates a proton by a β-elimination mechanism with reproduction of a chlorallylic structure, following which the process is repeated



where Nu is a nucleophile which can be a molecule of THF or another solvent.[127]

It was found by Myakov et al.[128] that PVC reacts with gallium trichloride with elimination of HCl at room temperature in the absence of a solvent. However, the degree of dehydrochlorination and the length of the resulting polyenes are small. Thus, for example, when the $GaCl_3$ content is 7.5%, the degree of dehydrochlorination only reaches 3%. With an increase in $GaCl_3$ content the degree of dehydrochlorination increases. In the UV spectra of the reaction products there are absorption bands at 317, 408, 470, and 535 nm, attributed to allylic, di-, tri- and tetra-enyl cations respectively. The formation of polyenyl cations in PVC macromolecules can be depicted by the following scheme:



(C)

The instability of PVC in the presence of $GaCl_3$ is due to the high ionising ability of $GaCl_3$ and also by the large energy gain in the elimination of HCl by the carbocation (C) through the formation of more stable allylic and polyenyl cations.[128]

On treatment of PVC in solution with different aromatic carbanions[129] obtained from organometallic compounds, the competing reactions of dehydrochlorination and nucleophilic substitution occur. The highest activity in dehydrochlorination was recorded for the phenylisopropyl carbanion $[C_6H_4(CH_3)_2C^-]$. According to UV spectroscopic data, the length of the resulting polyene sequences ranges from 5 to 12 conjugated C=C double bonds.[129]

When films of halogen-containing polymers under vacuum are brought into contact with antimony pentafluoride vapour, dehydrochlorination occurs vigorously to give long chains of conjugated double bonds.[130] On exposure of a PVDF film to SbF_5 vapour, the film darkens and then turns black. An increase of temperature was required in order to carry out the dehydrofluorination of polytrifluoroethylene, whereas a PVC flm turned black immediately on exposure to SbF_5 at room temperature. Taking into account the fact that SbF_5 is an effective dopant for polyacetylene,[86] it may be concluded that there is future potential in this method of dehydrohalogenation for obtaining organic semiconductor materials.

The reaction between PVC and the superoxide anion was studied by Osawa et al.[131,132] In order to achieve this, PVC in THF solution was treated with potassium superoxide in an atmosphere of nitrogen at 40 °C. In the IR spectra of the reaction products, absorption bands occur at 3300, 1680, 1620, and 765 cm^{-1}, attributed to hydroxyl groups, α,β-unsaturated keto groups, and polyene structures (1620 and 765 cm^{-1}) respectively. The UV spectroscopic data confirm the presence of conjugated polyene structures in the reaction products. According to the elemental analysis data, with an increase in the time of reaction between PVC and KO_2, the content of chlorine in the reaction products decreases while the oxygen content increases. In the opinion of the authors, initiation of the reaction between PVC and $O_2^{\cdot-}$ occurs by a mechanism involving nucleophilic substitution of the chlorine atoms in chlorallylic groups present in the initial PVC.[131,132] The resulting peroxide macroradicals undergo secondary reactions to form α,β-unsaturated keto groups, hydroxyl groups, peroxide cross-linking, and also polymer alkoxy radicals. The alkoxy radicals can detach a proton from the polymer chain to form alkyl macroradicals which undergo further dehydrochlorination to form conjugated polyene structures.[131,132]

In these studies[79,80,133] a method was proposed for the dehydrohalogenation of halogen-containing polymers [poly(α-chloroacrylonitrile,[79,80,133] PVC, chlorinated polybutadiene, poly(2,3-dibromobutene) [133]] by alkali metal hydrides in DMF or dimethyl sulphoxide solution at 60–80 °C to form polymers with a system of conjugated double bonds.

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The dehydrohalogenation products of halogen-containing polymers, as in the majority of polymers with a system of conjugation, have semiconductive properties and are of interest for their use in electrical engineering (sources of a current),[58,134,135] microelectronics ($p-n$ transitions, Schottky barriers, photoelectric cells[136]) optics (polarising films[137–144]), and also for the preparation of electrodes and membranes in electrochemistry, protective films in microwave technology,[145,146] and antistatic materials.[146,147]

The electrophysical properties of polymers with a system of conjugation obtained by dehydrohalogenation have been investigated in a considerable number of studies.[20,22,26,40,58,75,79,80,99,113,114,119–122,145–157] The specific electrical conductivity of the dehydrohalogenation products varies over a wide range ($10^{-12}-10^{-7}$ Ohm^{-1} cm^{-1}) depending on the nature of the initial polymer, the dehydrohalogenating agent, and the reaction conditions. Alloying (doping) of the reaction products with different electron-donating or electron-withdrawing components results in an increase in the electrical conductivity by a factor of 10^5-10^8 ($10^{-6}-10^{-1}$ Ohm^{-1} cm^{-1}). Iodine[20,22,26,40,119,120,122,150–152,154], $FeCl_3$,[26,151] SO_3,[58,119] BF_3,[26] AsF_5,[119] and also $(C_2H_5)_4NBF_4$ [156] and copper phthalocyanine[155] have been used as dopants.

From an examination of the results of the studies cited above it may be concluded that chemical dehydrohalogenation of halogen-containing polymers is a practicable and convenient method of obtaining carbon-chain polymers with a system of conjugation in the main chain, which can be used to obtain even crystalline polyacetylene.[158,159] The most effective dehydrohalogenating agents are hydroxides, alkoxides, and alkali metal amides. Dehydrohalogenation by DBU and SbF_5 also appears to have future potential.

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