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Thermal Decomposition and Stabilisation of Poly(vinyl Chloride)

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The kinetics and mechanism of the thermal dehydrochlorination of poly(vinyl chloride) and low-molecular-weight chlorohydrocarbons which model various fragments of the polymer molecule, are discussed. Studies designed to determine the qualitative and quantitative compositions of the unstable fragments in poly(vinyl chloride) macromolecules by ^{13}C NMR are examined. Attention is concentrated on the consideration of the mechanism of the action of the most effective thermostabilisers for the polymer-organotin compounds. The principal features of synergism in the stabilisation of poly(vinyl chloride) and the mechanism of the action of synergistic mixtures are analysed.
The bibliography includes 107 references.

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I. INTRODUCTION

Poly(vinyl chloride) (PVC) occupies one of the leading places in the world manufacture of polymeric materials. An important disadvantage of PVC is its instability towards various kinds of thermal and chemical influences. The thermal ageing of the polymer begins above 373 K.

The main principles of the ageing and stabilisation of polymers have been examined in Emanuel' and Buchachenko's book.[1] Various aspects of the problem of the thermal decomposition and stabilisation of PVC have been the centre of attention of many investigators. Studies on the ageing and stabilisation of PVC in Gorky are being pursued under the supervision of G.A.Razuvaev.

The aim of the present review is to analyse the present state of research into the main problems of the thermal decomposition and stabilisation of PVC. PVC belongs to the class of polymers which decompose under the influence of heat with elimination of side fragments from the macromolecules with the preferential formation of one low-molecular-weight product (namely HCl—more than 90%) and polyenes:

$$\sim(CH_2—CHCl)_n\sim \rightarrow mHCl + \sim(CH_2—CHCl)_{n-m}—(CH=CH)_m\sim;\quad n > m.$$

Despite the apparent simplicity of this overall reaction, investigators of the thermal decomposition of PVC have encountered extremely complex processes, some of the details of which still remain obscure.

II. THERMAL DECOMPOSITION OF LOW-MOLECULAR-WEIGHT MODEL COMPOUNDS

The experimental data (Table 1) on the thermal decomposition of compounds modelling various fragments of PVC macromolecules permit the following conclusions. In gaseous and liquid phases all chlorohydrocarbons decompose under the influence of heat with formation of HCl and an olefin (other products have not been detected). The kinetic curves for the decomposition of chlorohydrocarbons are described by first-order equations. In terms of the rate of their decomposition (or in terms of the corresponding rate constants), alkyl chlorides can be arranged in the sequence tertiary ≫ secondary ≫ primary.

Table 1. Arrhenius parameters and the temperature ranges of the thermal decomposition reactions of low-molecular-weight models of fragments of PVC macromolecules.

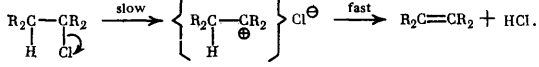
Model compound	$\lg A$, s^{-1}	E, kJ mol^{-1}	ΔT*, K	Phase	Refs.
Propyl chloride	13.45	230	693—751	gas	[2]
Pentyl chloride	13.80	232	683—723	»	[3]
s-Butyl chloride	13.75	210	612—663	»	[2]
t-Butyl chloride	12.40	173	563—614	»	[4]
3-Chlorobut-1-ene	13.34	203	593—683	»	[5]
4-Chlorohex-2-ene	10.75	142	523—586	»	[6]
6-Chlorohepta-2,4-diene	10.43	145	575—620	»	[7]
2-Chloro-2-methoxyethyl	11.46	140	453—523	»	[8]
8-Chlorohexadecane	10.55	151	509—557	liquid	[9]
8-Chloro-6-tridecylene	8.14	105	438—469	»	[9]
7-Chlorononа-3,5-diene	7.99	81	343—369	»	[9]

*ΔT = temperature range of the decomposition reaction.

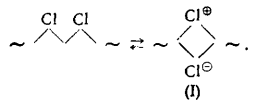
The activation energy for the thermal decomposition of secondary derivatives is lower by 21—33.5 kJ mol^{-1} and that of tertiary degrees is lower by 29—33.5 kJ mol^{-1} than the activation energy for the decomposition of primary derivatives. The reaction is greatly accelerated by the presence of a non-terminal double bond in the β-position relative to the chlorine atom. If the carbon—carbon bond is located at the end of the molecule (as in 3-chlorobut-1-ene), then the activation energy for the thermal decomposition of this compound is much higher than for a compound with an internal double bond (as in 4-chlorohex-2-ene) and is only slightly lower than the activation energy for the thermal decomposition of secondary-chlorohydrocarbons. An alkoxy-group

in the α-position relative to the chlorine has an appreciable accelerating effect on the thermal decomposition of the chlorohydrocarbon (Table 1).

There is no rigorous evidence in the literature concerning the elementary steps in the thermal dehydrochlorination of the chlorohydrocarbons presented in Table 1. The absence of compounds other than HCl and an olefin, the absence of an appreciable retarding effect by free radical inhibitors on the thermal decomposition of the chlorohydrocarbons listed in Table 1, a marked accelerating effect of nucleophilic substituents (groups with a carbon–carbon double bond and alkyl and alkoxy-groups in the α-position relative to the carbon–carbon bond), and the acceleration of the thermal decomposition of chlorohydrocarbons in the liquid phase with increase of the polarity and basicity of the solvent have been established experimentally.[2–10] All these factors suggested[2,8] that the thermal decomposition reactions of chlorohydrocarbons are two-stage processes of type E1 (unimolecular elimination reactions) and that the first and rate-determining stage is an intense polarisation (partial ionisation but not dissociation) of the C–Cl bond:



It has been recently suggested[11] that the primary elementary step in the thermal dehydrochlorination of chlorohydrocarbons which model the PVC molecule is the formation of cyclic chloronium ions:



(I)

It has been shown[11,12] that a large amount of olefin (~30%) and HCl is formed in the liquid phase during the thermal decomposition of a chlorohydrocarbon containing in its molecule one chlorine atom (7-chlorotridecane) in the presence of dodecane-1-thiol or 9,10-dihydroanthracene. The thermal decomposition of chlorohydrocarbons containing two or three chlorine atoms per molecule (4,6-dichloro-n-nonane, 2,4,6-trichloro-n-heptane) in the presence of the same chain transfer agents yields only the chlorohydrocarbon reduction product. Thus different products are formed from monochlorohydrocarbons, on the one hand, and from dichloro- and trichlorohydrocarbons, on the other.

It has been shown[11,12] that the thermal decomposition of polychlorohydrocarbons, modelling the fragments of PVC macromolecules, in the presence of thiols involves the reaction

$$\sim CH_2{-}CHCl\sim + 2RSH \rightarrow \sim CH_2{-}CH_2\sim + RSSR + HCl; \quad R = Alk, Ar. \qquad (1)$$

The composition of the reaction products, in particular the presence of a disulphide, indicates a free-radical process mechanism.

Depending on the reaction conditions, the cyclic chloronium ion (I) can decompose both via a free-radical mechanism (in the presence of an electron donor and an effective chain transfer agent) and via an ionic-molecular mechansim.[11] There is also a possibility of a radical-chain mechanism of the thermal decomposition of polychlorohydrocarbons in the presence of active chain transfer agents, which include thiols and 9,10-dihydroanthracene.

The effective activation energy for a radical chain reaction with quadratic chain termination is described by the expression[12]

$$E_{eff} = \tfrac{1}{2}E_i + E_p - \tfrac{1}{2}E_t,$$

where E_i is the activation energy for the initiation step (approximately equal to the energy of the C–Cl bond dissociated), E_p the activation energy for the most endothermic chain propagation stage, and E_t the activation energy for chain termination. E_i and E_p make the greatest contribution to E_{eff}.

The C–Cl bond energy ($\sim E_i$) in chlorohydrocarbons having the structure $\sim(CH_2 - CHCl)_n\sim$ is 326.6 kJ mol^{-1}, while in compounds of the type $\sim(CH{=}CH)_m{-}CHCl\sim$ it amounts to 234.5–251.2 kJ mol^{-1}.[13] The most endothermic chain propagation stages are as follows:[14]

$$\sim CHCl{-}\dot{C}H{-}CHCl\sim \rightarrow \sim CHCl{-}CH{=}CH\sim + Cl^{\cdot}; \qquad (2)$$

$$\sim CH_2{-}\dot{C}Cl{-}CH_2\sim \rightarrow \sim CH{=}CCl{-}CH_2\sim + H^{\cdot}. \qquad (3)$$

Stage (2) is 83.7 kJ mol^{-1} endothermic and stage (3) is 163.3 kJ mol^{-1} endothermic.[14] After adding together $1/2E_i$ and E_p, neglecting E_t, we obtain E_{eff} = 326.6 kJ mol^{-1} for compounds of the type $\sim(CH_2 - CHCl)_n\sim$ and E_{eff} = 280.5–283.9 kJ mol^{-1} for $\sim(CH{=}CH)_m{-}CHCl\sim$.

For the thermal decomposition of chlorohydrocarbons in the liquid phase in the presence of active chain transfer agents (for example, of thiols) the most endothermic stages (2) and (3) do not occur because the free radicals react with the thiol and the effective activation energy for the thermal decomposition of hydrocarbons becomes equal to approximately half the C–Cl bond energy. Consequently, owing to the decrease of E_{eff} in the presence of active chain transfer agents, there is an increased probability of the decomposition of the chlorohydrocarbons via a radical chain mechanism.

The difference between monochlorohydrocarbons and polychlorohydrocarbons consists in the fact that the thermal decomposition of the latter involves the formation of the polyenes $\sim(CH{=}CH)_m{-}CHCl\sim$, in which the C–Cl bond energy is lower by ~83.7 kJ mol^{-1} than the energy of the same bond in monochlorohydrocarbons. Consequently, they are also characterised by a lower value of E_{eff} for thermal decomposition via a radical chain mechanism.

Thus the radical mechanism for the thermal decomposition of polychlorohydrocarbons which model the fragments of PVC macromolecules can compete with the ionic-molecular mechanism only in the presence of electron donors and active chain transfer agents. In the absence of such additives, the ionic-molecular mechanism predominates.

III. KINETICS OF THE THERMAL DECOMPOSITION OF POLY(VINYL CHLORIDE)

The thermal decomposition of PVC in the presence of HCl is an autocatalytic process.[15–26] Conditions under which critical phenomena are observed have been formulated and equations for the kinetics of the thermal decomposition of the polymer in a closed volume with removal of HCl have been derived.[15,22] The critical size of the polymer specimen, i.e. the maximum thickness of the film for which autocatalysis does not yet develop, is very small:[22] 0.24 mm at 463 K, 0.18 mm at 473 K, and 0.15 mm at 483 K. Hence it follows that correct data for the kinetics of the thermal decomposition of PVC, uncomplicated by autocatalysis, can be obtained only by employing a polymer in the form of a thin layer of powder or a film in a high vacuum. In addition, autocatalysis can be excluded by decomposing PVC in solution, but the solvent must not then exert a significant influence on the dehydrochlorination process.[24]

Fig. 1 presents experimental data for the thermal decomposition of PVC in the form of a thin layer of powder under high vacuum[27] and Fig. 2 illustrates the kinetic curves for the dehydrochlorination of the polymer in solution in 1,2,4-trichlorobenzene.[24] The dehydrochlorination process consists of two stages: initially the rate of reaction falls and after a certain time becomes virtually constant. This shows that unstable fragments of the macromolecules are decomposed initially and, after the complete decomposition, the rate of dehydrochlorination is determined by the decomposition of only the normal units of the PVC macromolecules. An increase in the initial concentration of the unstable fragments leads to an increased initial rate of dehydrochlorination of PVC and hardly affects the steady-rate of the process (Fig. 2).[24]

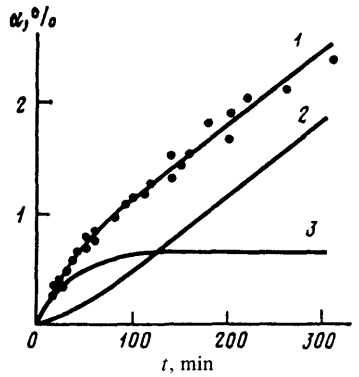


Figure 1. Kinetic curves for the dehydrochlorination of PVC *in vacuo* (~10–2 Pa) at 473 K and with constant freezing out of HCl: 1) experiment; 2) calculation by Eqn. (19); 3) result of the graphical subtraction of curve *2* from curve *1*;[27] α = degree of conversion.

Effective rate constants have been determined for the thermal decomposition of the unstable chloroallyl (k^1_{eff}) and ketochloroallyl (k_π) fragments:

$$k^1_{eff} = 10^{9.6\pm0.5} \times e^{-28000\pm1000/RT}\ s^{-1}\ \text{(Refs. 17, 27)},$$
$$k_\pi = 10^{14.9\pm0.8} \times e^{-35100\pm1700/RT}\ s^{-1}\ \text{(Ref. 26)},$$

as well as normal PVC units:

$$k^0_{eff} = 10^{11.8\pm0.5} \times e^{-38000\pm1000/RT}\ s^{-1}\ \text{(Refs. 17, 27)},$$
$$k_0 = 10^{3.4\pm0.7} \times e^{-21500\pm1500/RT}\ s^{-1}\ \text{(Ref. 26)},$$

where k_0 is the rate constant for the thermal decomposition of the normal units and k^0_{eff} the effective rate constant for their decomposition.

An important characteristic of the thermal decomposition of PVC is the length of the kinetic chain. The average length of the kinetic chain l_{av} can be determined from experimental data on the thermal decomposition of PVC containing unstable fragments at a known concentration by a simple division of the total amount of HCl evolved in the decomposition of all the unstable fragments by their initial concentration. It follows from the literature[24,28] that l_{av} = 4–10. This value of l_{av} is greater than the average number of conjugated double bonds in the polyenes formed, which is 3–5 according to ultraviolet spectroscopic determinations.[24,29] This is associated with the participation of the polyenes in the secondary intra- and inter-molecular cyclisation reactions,[11,20,24,29] which decreases the average number of conjugated double bonds.

The thermal decomposition of "ideal" PVC which contains no unstable fragments can be represented by the following equations[17,25,27]

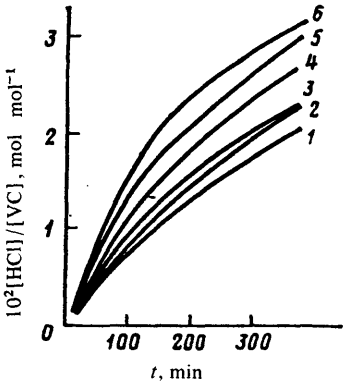


Figure 2. Kinetic curves for the thermal decomposition of PVC (1% solution in 1,2,4-trichlorobenzene) at 473 K for different initial contents of chloroallyl groups (mole %): 1) 0.006; 2) 0.012; 3) 0.017; 4) 0.036; 5) 0.069; 6) 0.107;[24] VC = vinyl chloride.

Initiation:

$$\sim(CH_2{-}CHCl)_n{\sim} \xrightarrow{k_0} HCl + \sim(CH_2{-}CHCl)_{n-1}{-}(CH{=}CH){\sim}. \quad (4)$$

Chain propagation:

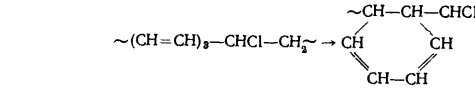
$$\sim(CH_2{-}CHCl)_{n-1}{-}(CH{=}CH){\sim} \xrightarrow{k_1} HCl + \sim(CH_2{-}CHCl)_{n-2}{-}(CH{=}CH)_2{\sim}; \quad (5)$$

$$\sim(CH_2{-}CHCl)_{n-2}{-}(CH{=}CH)_2{\sim} \xrightarrow{k_2} HCl + \sim(CH_2{-}CHCl)_{n-3}{-}(CH{=}CH)_3{\sim}; \quad (6)$$

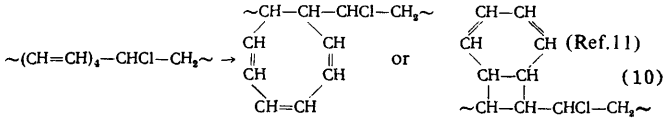
$$\sim(CH_2{-}CHCl)_{n-3}{-}(CH{=}CH)_3{\sim} \xrightarrow{k_3} HCl + \sim(CH_2{-}CHCl)_{n-4}{-}(CH{=}CH)_4{\sim}; \quad (7)$$

$$\sim(CH_2{-}CHCl){-}(CH{=}CH)_{n-1}{\sim} \xrightarrow{k_{n-1}} HCl + \sim(CH{=}CH)_n{\sim}. \quad (8)$$

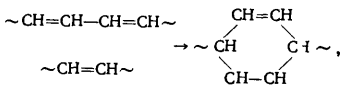
Chain termination:



; (9)



(10)

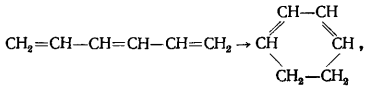


(11)

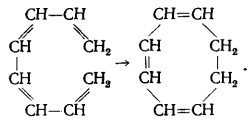
where $n = l_{av}$.

Reaction (4) represents the statistical initiation of the elimination of HCl from any unit of the macromolecules.

The occurrence of the termination reactions (9) and (10) has been confirmed by experiments with low-molecular-weight model compounds. The occurrence of the following cyclisation reactions of trienes and tetraenes has been demonstrated:[30,31]



(12)



(13)

Reactions (12) and (13) are described by first-order kinetic equations with the Arrhenius parameters $\lg A = 11.0$ and $E = 125$ kJ mol^{-1} for reaction (12)[30] and $\lg A = 11.0$ and $E = 71$ kJ mol^{-1} for reaction (13).[31]

The intermolecular polyene cyclisation reaction (11) leads to the formation of a cross-linked polymer.[19]

On the basis of the scheme presented above, the rate of evolution of HCl can be expressed by the equation[17,27]

$$\frac{d[HCl]}{dt} = k_0c_0 + k_1c_1 + k_2c_2 + \ldots + k_nc_n, \quad (14)$$

where k_0, k_1, ..., k_n are the rate constants for different stages, c_0, c_1, c_2, ..., c_n are the concentrations of the corresponding fragments, and $n = l_{av}$.

Using the theory of consecutive reactions,[32] we shall express c_0, c_1, c_2, ..., c_n at time t in terms of c_0^0 (the initial concentration of the ~CH_2–CHCl~ fragments in the polymer) and the rate constants k_0, k_1, ..., k_n:

$$c_0 = c_0^0 e^{-k_0t}, \quad (15)$$

$$c_1 = c_0^0\left[\frac{k_0}{k_1 - k_0}e^{-k_0t} + \frac{k_0}{k_0 - k_1}e^{-k_1t}\right], \quad (16)$$

$$c_2 = c_0^0\left[\frac{k_0k_1}{(k_1 - k_0)(k_2 - k_0)}e^{-k_0t} + \frac{k_0k_1}{(k_0 - k_1)(k_2 - k_1)}e^{-k_1t} + \frac{k_0k_1}{(k_0 - k_2)(k_1 - k_2)}e^{-k_2t}\right] \text{ etc.} \quad (17)$$

Having substituted the value of c_0, c_1, c_2, etc. [Eqns. (15)–(17)] in Eqn.(14), subject to the condition $k_0 \ll k_1 \ll k_2 \cong k_n$ (this has been demonstrated for model compounds[2–10]), we arrive at a greatly simplified formula:[17,27]

$$\frac{d[HCl]}{dt} = k_0c_0^0 l_{av}\left(e^{-k_0t} - \frac{l_{av} - 1}{l_{av}}e^{-k_1t}\right). \quad (18)$$

Integration of Eqn.(18) yields an expression for the concentration of HCl:

$$[HCl] = l_{av}c_0^0(1 - e^{-k_0t}) - (l_{av} - 1)c_0^0\frac{k_0}{k_1}(1 - e^{-k_1t}). \quad (19)$$

It can be shown that $k_{eff}^0 = k_0l_{av}$ and $k_{eff}^1 = k_1l_{av}$.[17,27] Knowing k_{eff}^0, k_{eff}^1, and l_{av}, it is possible to determine k_0 and k_1. The constants k_0, k_1, and l_{av} obtained by different workers[17,24,27,33,34] are listed in Table 2.

Comparison of Tables 1 and 2 shows that the rate constants for the decomposition of fragments of the PVC macromolecules are close to the rate constants for the thermal decomposition of the model compounds in the liquid phase.

Having substituted the values of k_0, k_1, and l_{av}[17,27] in Eqn.(19), it is possible to calculate the time variation of the HCl concentration in the decomposition of the "ideal" polymer which does not contain unstable fragments (Fig.1, curve *2*). The existence of a certain initial section of curve *2* where the rate of formation of HCl increases is striking. After that, the rate no longer changes. The increase in the rate of formation of HCl is associated with the accumulation and decomposition of fragments containing carbon–carbon double bonds: initially the rate of accumulation of such fragments is greater than the rate of decomposition but afterwards the two rates approach one another and equilibrium is attained at a constant concentration of the chloroallyl fragments. The equilibration time depends on the rate constant ratio k_0/k_1, which follows from Eqn.(19).

Table 2. Arrhenius parameters for the thermal decomposition reactions of fragments of PVC macromolecules.

Polymer fragment	$\lg A$, s^{-1}	E, kJ mol^{-1}	Phase	ΔT, K	l_{av}	Refs.
~CH_2–CHCl~	11.0	159	polymer melt	453—523	8	[17, 27]
~CH=CH–CHCl–CH_2~	9.8	113	ditto	453—483	8	[17, 27]
~CH_2–CHCl~	3.4	90	»	418—448	—	[34]
~CH=CH–CHCl–CH_2~	—	—	»	453	8	[33]
~CH=CH–CHCl–CH_2~	—	—	polymer solution	473	10—13	[24]

Fig.1 demonstrates the discrepancy between the experimental curve *1* and the theoretical curve *2* calculated by Eqn.(19). This means that the initial rate of thermal decomposition of PVC is determined not only by the statistical decomposition of the normal units of the macromolecule but also by the thermal decomposition of unstable fragments always present in the initial polymer. Graphical subtraction of curve *2* from curve *1* yields the kinetic curve for the thermal decomposition of the unstable fragments alone (curve *3*).

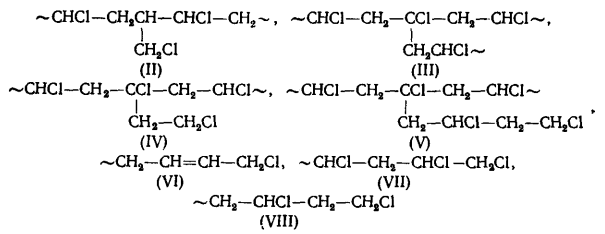
Fig.1 clearly illustrates the contribution of two thermal decomposition processes, initiated by the statistical decomposition of the normal units (curve *2*) and the unstable fragments (curve *3*), to the overall dehydrochlorination reaction of real PVC as a function of time. Knowing l_{av} and the amount of HCl evolved in the decomposition of all the unstable fragments (which can be readily determined from curve *3* in Fig.1), it is possible to estimate the concentration of the unstable fragments in PVC. For the PVC specimen whose thermal decomposition is illustrated in Fig.1, it amounts to ~0.08 mole %.

IV. THE NATURE OF THE UNSTABLE FRAGMENTS IN POLY(VINYL CHLORIDE) MACROMOLECULES

The controversy concerning the nature and concentration of the unstable fragments in PVC macromolecules and also the contribution of each of them to the initial rate of thermal decomposition of the polymer has continued for a long time.[7,9–11,15,24,28,29,33–50] The difficulty of the solution of this problem consists in the fact that the unstable fragments are present in the polymer at low concentrations.

The concentration of double bonds in PVC has been determined by the bromination[36,44] and ozonolysis[24,33,34,40] methods as 0.1–0.5 mol %. By combining the ozonolysis method with hydrolysis and subsequent determination of the molecular weight distribution (MWD) of the polymer[24,33,40] by ^{13}C NMR[44,47] and other procedures,[39] it was established that PVC contains 0.01–0.05 mole % of internal chloroallyl fragments. The bulk of the double bonds in PVC are located either at the ends or near the ends of the macrochains.

The question of the presence of a chlorine atom at a tertiary carbon atom in PVC has been the subject of controversy for many years. A convenient method has been developed[11,35] for the reduction of PVC to polyethylene using Bu_3SnH or Bu_3SnD as the reducing agent. Analysis of the ^{13}C NMR spectra of the reduced PVC demonstrated the presence of the following fragments in the polymer:[11,35,43,44]



The contents of the fragments (II)–(V) in different PVC specimens are presented in Table 3.

Table 3. Concentrations of branched structures in PVC macromolecules.[35]

Brand of PVC	T_p, K*	No. of fragments per 1000 monomer units			
		(II)	(III)	(IV)	(V)
A	373	4.0	0.6	1.6	1.8
B	373	4.4	0.8	1.4	1.6
S-54	348	5.6	0.6	1.2	2.0
E-54	348	4.4	0.6	0.6	1.0
P-23	329	4.2	0.4	0.2	0.4
S-80	316	4.4	0.4	0.6	1.4
E-80	316	4.0	0.6	1.0	1.2
103EP	—	5.2	0 4	0.6	1.2

*T_p = polymerisation temperature of vinyl chloride.

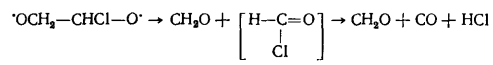
For different brands of PVC, obtained at temperatures ≤348 K, the overall concentration of the fragments containing a chlorine atom at a tertiary carbon atom is 0.1–0.28 mole %.[11,35,43,44]

PVC contains smaller amounts (0.01 mole %) of peroxy- and hydroperoxy-groups[33,36–38] and up to 0.02 mole % of internal fragments with a "head-to-head" structure.[48]

It has been demonstrated on model compounds that the peroxy- and hydroperoxy-groups as well as units of the polymer chain containing a chlorine atom in the allyl position (~CH=CH–CHCl–CH_2~) or at a tertiary carbon atom are unstable fragments of PVC macromolecules which readily decompose,[22–10,46] A group of investigators have carried out special experiments designed to synthesise PVC specimens containing low concentrations of the above unstable fragments.[24,28,33,45] It has been shown that an increase in the concentration of the internal chloroallyl fragments,[24,33,39,40,45] groups with chlorine atoms at a tertiary carbon atom,[28,43,44] and peroxy- and hydroperoxy-fragments[33,37,38] in the polymer appreciably increases the initial rate of thermal decomposition of the polymer.

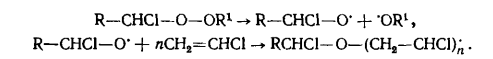
The formation of all the unstable fragments in the initial PVC is determined by the characteristic features of the radical polymerisation of vinyl chloride and their quantitative content is directly related to the technological parameters of a specific process: the purity of the monomer, the concentration and nature of the initiator, the polymerisation temperature, the amount of oxygen present in the system, the type and concentration of the emulsifying agent, the suspension stabiliser and other additives, the degree of completion of the polymerisation process, the degree of purification of the water used, etc.

The presence of oxygen in the polymerisation of vinyl chloride leads to the formation of polymeric peroxides and hydroperoxides.[33,38,51] Their decomposition via the general mechanism[33,38,51]



takes place simultaneously with the formation reaction. After polymerisation, up to 20–30% peroxy- and hydroperoxy-groups remain undecomposed in the polymer.[38]

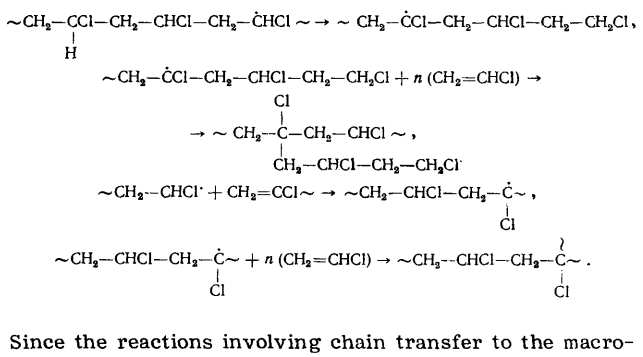
In the decomposition of polymeric peroxides in the presence of an excess of the monomer, i.e. under the conditions of the polymerisation of vinyl chloride, there is a possibility that fragments of the polymeric peroxides are incorporated as end groups in the PVC macromolecule:



Judging from the parameters of the thermal decomposition of model compounds containing an alkoxy-group in the α-position relative to the C–Cl bond, the RCHCl–OR^1 fragments can also be classified as unstable groups in PVC macromolecules (Table 1).

It has been established[50] that the polymer formed on polymerisation of vinyl chloride under the conditions of a reduced pressure of the monomer contains a greater amount of unstable fragments, in particular branched structures with a chlorine atom at a tertiary carbon atom, and its thermal stability is lower.

The following mechanisms have been proposed for the formation reactions of the branched fragments with mobile chlorine atoms:[11,35]



Since the reactions involving chain transfer to the macromolecule in the polymerisation of vinyl chloride compete with the chain propagation reactions, whose rate is determined by the concentrations of the macroradicals and the monomer, it follows that the rate of the interaction of the macroradicals with the polymer molecule and the probability of the formation of unstable fragments increase with decrease in the monomer concentration.

Thus it has now been established that, in the usual brands of PVC, the highest concentration of unstable fragments is that of chlorine atoms at the branching sites (0.1–0.28 mole %). Consequently they should in fact exert a decisive influence on the initial rate of thermal decomposition of the polymer.[11,35,43,44] The quantitative contribution of other unstable groups (peroxy-, hydroperoxy-, and chloroallyl) and possibly also fragments of the type ~CH_2–CCl(OR)~ and ~O–CH=CH–CHCl~ to the initial rate of thermal decomposition of the polymer remains obscure. The influence of conditions in the polymerisation of vinyl chloride on the quantitative content of each unstable fragment in the polymer has not been adequately investigated.

The role of the ~C(O)–CH=CH–CHCl~ fragments in the thermal decomposition of PVC is not considered in this review, since this question has been discussed exhaustively in a recently published book[42] and review.[34]

V. THE MECHANISM OF THE THERMAL DECOMPOSITION OF POLY(VINYL CHLORIDE) IN THE ABSENCE OF HCl

There exist two theories of the thermal decomposition of PVC: the ionic-molecular[11,17,24,33,41] and radical[37,52,53] theories. According to the radical theory, the principal active species involved in the chain propagation reactions is atomic chlorine. Metals behave as effective acceptors of atomic chlorine. Mercury and silver (metals which do not interact with HCl) do not affect the rate of dehydrochlorination of PVC *in vacuo* after being added to the polymer even in large amounts (in 1 : 1 proportions by weight).[16] Mercury vapour does not retard the thermal decomposition of PVC in the absence of HCl either.[52] These findings show that the thermal decomposition of PVC proceeds mainly via an ionic-molecular mechanism. Data for the thermal decomposition of model compounds in the liquid phase (Section II) also serve as an argument in support of the ionic-molecular mechanism.

The occurrence of radical processes in the thermal decomposition of the polymer is indicated by the following experimental data. Apart from HCl, benzene is evolved in small amounts in the reaction (a factor of 100–1000 less then HCl), its yield diminishing in the presence of free radical inhibitors such as nitric oxide and α-naphthol.[22,52] The peroxides and hydroperoxides present at low concentrations in the polymer increase the initial rate of thermal decomposition of PVC.[33,37,53] However, it has been shown by the inhibitor method that the formation of HCl via the radical mechanism is a process involving very short chains (the chain length is ~2).[52] It follows from the experimental data for the thermal decomposition of PVC containing a specified amount of polymeric peroxides[33] that the average chain length of the radical dehydrochlorination reaction is ~2. This agrees with the above results.[52] The short chain length (~2) is apparently associated with the endothermic nature of the chain propagation stages (2) and (3), which hinders the radical chain process.

Thus the thermal decomposition of PVC in the absence of HCl proceeds mainly via the ionic-molecular mechanism complicated by radical reactions.

VI. THE MECHANISM OF THE AUTOCATALYTIC DECOMPOSITION OF THE POLYMER

The autocatalysis of the thermal decomposition of PVC is explained by the interaction of HCl with polyenes.[16,18,21,54] Definite information about the mechanism of this process is provided by experiments on its retardation by compounds which do not interact with HCl.[16,17,19–21,55–61] The stabilising effect of these compounds cannot be explained by the destruction of the catalyst.

Catalysis is not observed in the thermal decomposition of PVC powder in sealed evacuated bulbs in the presence of maleic anhydride, although HCl does accumulate in the bulbs.[21,55] The autocatalytic decomposition of PVC is suppressed by mercury, silver (in the form of a finely dispersed powder mixed with the polymer particles),[16,52,57] trialkylsilanes,[58,59] and the chlorides of coordination-unsaturated metals at microconcentrations.[17,56,60,61]

We shall now discuss the experimental data obtained from the standpoint of the radical and ionic theories of the autocatalytic decomposition of PVC. As shown in Section II, in the presence of active chain transfer agents, the probability of the radical thermal decomposition reactions of polychlorohydrocarbons should increase as a consequence of the suppression of the most endothermic chain propagation stages (2) and (3). Hydrogen chloride is a low-molecular-weight compound which readily diffuses in PVC and can play the role of a chain transfer agent and hence increase the rate of the radical chain thermal decomposition reaction of the polymer.

Mercury and silver can accept chlorine atoms; they should inhibit the radical thermal decomposition of PVC. However, from the standpoint of the radical chain dehydrochlorination of PVC in the presence of HCl, it is difficult to account for the suppression of the autocatalytic dehydrochlorination of PVC by maleic anhydride and metal chlorides at microconcentrations and also the fact that the usual inhibitors of free-radical reactions, namely toluene, diphenylmethane, and sterically hindered phenols, do not have an appreciable retarding effect on the autocatalytic decomposition of the polymer.[20,21,52,62] Maleic anhydride enters into the Diels–Alder reaction, but only with dienes having the cisoid structure. However, polyenes with the transoid configuration remain in the polymer and the radical chain process should therefore have developed. The chlorides of coordination-unsaturated metals react with polyenes to form paramagnetic charge-transfer complexes[63] whose involvement in the inhibition of radical reactions is difficult to explain.

The radical chain theory of the autocatalytic decomposition of PVC also fails to explain the absence of a catalytic influence of HCl on the thermal decomposition of poly(vinylidene chloride) (PVDC),[17,20,23,64,65] a polymer whose chemical structure is close to that of PVC, and the accelerating effect of Cl_2 and Br_2 on the thermal decomposition of PVC, while no such effect is observed in the thermal decomposition of PVDC.[64]

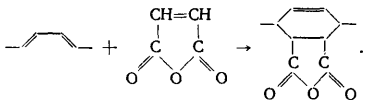
The available experimental data can be accounted for by assuming that the interaction of HCl with polyenes results in the formation of charge-transfer complexes (CTC) in which the polyene behaves as the donor and HCl as the acceptor, the HCl reacting predominantly with polyenes having the cisoid structure:[17,27]



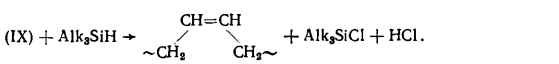
$[ClHCl]^{\ominus}$
(IX)

The complex $H^{\oplus}[ClHCl]^{\ominus}$ is a stronger electron acceptor than HCl, since the energy gain on formation of $[ClHCl]^-$ is 79.2 kJ mol^{-1}.[66] The ion pairs (IX) initiate the thermal decomposition of PVC via a heterolytic mechanism.

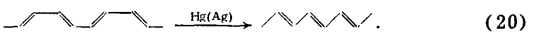
The inhibiting effect of maleic anhydride on the autocatalytic decomposition of PVC can be explained by the Diels–Alder reaction with *cis*-polyenes:



Trialkylsilanes reduce compound (IX) via the reaction[17]



The mercury and silver atoms interacting with polyenes can play the role of catalysts of the *cis–trans* isomerisation of the latter:



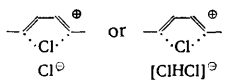
(20)

trans-Polyenes are thermodynamically more stable at 440–480 K than the *cis*-polyenes, since it is known[67] that, on heating above 373 K, *cis*-polyacetylene is converted into *trans*-polyacetylene.

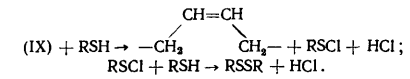
The paramagnetic CTC of the chlorides of coordination-unsaturated metals with polyenes can also play the role of catalysts of reaction (20).

The thermal decomposition of PVDC leads to the formation of polyenes with bulky electron-accepting substituents (chlorine atoms), which hinders their interaction not only with HCl but also with Cl_2 and Br_2. For this reason, these additives do not show an accelerating effect.[64]

The catalytic effect of Cl_2 and Br_2 on the thermal decomposition of PVC[64] can also be accounted for by the formation of an active intermediate species (ion pair) on interaction of the *cis*-polyene with the additive:



It may be that the reaction (1) of thiols with chlorohydrocarbons[11] also proceeds via the mechanism



In contrast to monochlorohydrocarbons, polychlorohydrocarbons give rise to polyenes on thermal decomposition, which interact with the acceptor (HCl) more readily than compounds with a single double bond.

Some workers believe that the autocatalysis is associated with the influence of HCl on the decomposition of the normal PVC units.[15,22,52]

Experimental data obtained recently lead to the conclusion that the autocatalytic decomposition of PVC in the presence of HCl has an ionic mechanism.[15,17,52,54]

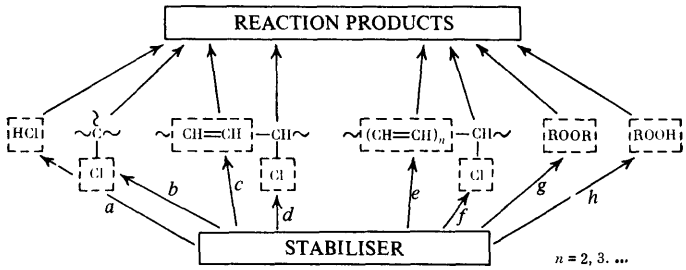
VII. THE MECHANISM OF THE ACTION OF EFFECTIVE STABILISERS OF POLY(VINYL CHLORIDE) IN ITS THERMAL DECOMPOSITION

The following procedures for reducing the rate of the autocatalytic decomposition of PVC follow from the ideas concerning the influence of HCl on the decomposition of the polymer: (1) by binding the HCl; (2) by interaction of the stabiliser with the double bonds (conjugated double bonds), and (3) by inhibition of the heterolytic chain reaction as a result of the deactivation of the ion pairs.

The initial rate of the non-catalytic decomposition can be reduced by reducing the concentration of the unstable fragments and the chain length l_{av} in the consecutive dehydrochlorination reaction.

It follows from Scheme 1 that the stabilisation of PVC is based on reactions of the stabiliser with HCl (*a*), reactions involving the nucleophilic substitution of the labile chlorine atoms by groups which are more strongly bound to the polymer (*b*, *d*, and *f*), reactions involving the addition to double (*c*) and conjugated double (*e*) bonds, and the decomposition of peroxides and hydroperoxides (*g* and *h*).

Scheme 1



The classification of stabilisers of PVC can be based on different features. It has been suggested that stabilisers be divided into two groups: (1) stabilisers acting on the non-catalytic HCl formation reaction and (2) stabilisers preventing the catalytic dehydrochlorination.[52] A method has been developed for determining the critical concentration of the HCl acceptors.[52,68] The classification based on the chemical structures of the stabilisers has been most widely adopted.

A classification of the PVC thermostabilisers based on their reactivities towards the units of the macrochains has also been proposed.[17]

The first group includes Group IA and IIA metal carboxylates,[20,68–70] compounds of the type R_4Sn (R = alkyl or aryl) and Ph_4Pb,[20] organic phosphites,[20,69,71,72] epoxy-compounds,[42,69] maleic anhydride (acid), maleate esters,[20,21,55,69,73,74] organosilicon and organogermanium hydrides,[58,59] oligosilanes,[75] and other compounds.[69] It has been shown[17,20,21,55,58,59,71,75] that the main stabilising function of the above compounds consists merely in reducing the rate of the autocatalytic decomposition of the polymer. The rate of the thermal decomposition of PVC in the presence of such stabilisers at best approaches the rate of its non-catalytic dehydrochlorination. These stabilisers are relatively inactive in nucleophilic substitution reactions (Scheme 1, reactions *b*, *d*, and *f*).

The second group includes the most effective PVC thermostabilisers: organotin derivatives of maleic and thioglycolic acids having the structures R_2SnX_2, $R_2Sn(OOCCH{=}CHCOO)$, and R_3SnX, where R = alkyl, X = OOCCH=CHCOOR, or SCH_2COOR,[20,69,76–83] as well as multicomponent synergistic mixtures based on Ca–Zn and Ba–Cd carboxylates.

Organic acid (except for maleic and thioglycolic acids) salts of dialkyltin, trialkyltin carboxylates,[20,69,83] triaryltin isocyanates,[84] cadmium carboxylates,[20,69,70,85] binary synergistic mixtures including zinc, cadmium, or dialkyltin carboxylates as well as an organic phosphite,[20,69,71,72] an organotin compound and an organic phosphite,[20,86] an organolead compound and an organic phosphite,[87] an organic phosphite and the chloride of a coordination-unsaturated metal,[20,71] an organosilicon or an organogermanium hydride and the chloride of a coordination-unsaturated metal,[88] the carboxylate of a coordination-unsaturated metal and a compound with OH, SH, and NH groups,[89–95] as well as ternary synergistic mixtures consisting of Ca–Zn carboxylates and a polyol, Ba–Cd

carboxylates and a polyol,[89,91,93-96] Group II metal carboxylates and epoxy-compounds,[42,69,97,98] and others[42,69] approach the second group in terms of the efficiency of their action.

In the presence of the above stabilisers the rate of dehydrochlorination of the polymer is several times lower [in the best case, in the presence of bis(alkyl maleate)dialkyltin derivatives, by a factor of 8[76]] than the rate of the non-autocatalytic decomposition of PVC. The efficiency of the action of the stabiliser is characterised by a period T from the start of decomposition in the presence of the stabiliser to the sharp increase in the rate of dehydrochlorination of PVC. In the thermal decomposition of PVC in the presence of stabilisers belonging to the second group, no colour change is observed during the period T and a cross-linked polymer is not formed. The stabilisers of this group participate in all the reactions indicated in Scheme 1.

The third group includes zinc carboxylates,[69,89-96] triphenyl-lead isocyanate,[87] organotin compounds having the structures $Ph_2Sn(OOCCH{=}CHCOO)$, Ph_2SnX_2, $RSnX_3$, and $R_2Sn(SCH_2COO)$, where R = alkyl and X = OOCCH=CHCOOR or SCH_2COOR,[69,76,83] and other compounds. They too are effective PVC stabilisers, but, in terms of the period T, they are appreciably inferior to compounds of the second group. Their characteristic feature is the formation, in the interaction with HCl and with fragments of the macrochains, of metal chlorides which are powerful catalysts of the dehydrochlorination of the polymer and of the reaction of the stabiliser with the normal units. This leads to the rapid consumption of the stabiliser and hence to the shortening of the period T.

In recent years much attention has been devoted to the study of the mechanism of the action of organotin compounds[11,17,34,42,69,76-83] and synergistic mixtures,[11,17,42,69,86-99] which effectively stabilise polymers and are widely used in practice.

1. Organotin Compounds

(a) Kinetics of the Thermal Decomposition of PVC in the Presence of Organotin Derivatives of Maleic and Thioglycolic Acids

We shall consider the kinetics of the thermal decomposition of PVC in the presence of the most effective stabilisers—organotin derivatives of maleic and thioglycolic acids. As an example, Fig. 3 presents the kinetic curve (curve 3) for the accumulation of ionic chlorine in the thermal decomposition of the polymer in the presence of $Bu_2Sn(OOCCH{=}CHCOOC_6H_{11})_2$. Three sections can be distinguished in the curve: along the first section, the rate continually diminshes, along the second it is constant, and along the third it rises sharply.

The initial section of the kinetic curve corresponds to the interaction of the unstable fragments with the stabiliser. The presence of the stationary section shows that all the unstable units of the initial polymer have reacted with the stabiliser and a constant rate of thermal decomposition, initiated by the statistical disruption of the normal units of the macrochain, is established. The acceleration of the dehydrochlorination of PVC along the third section of curve 3 (Fig. 3) is caused by the development of the catalytic decomposition of PVC.

It has been demonstrated by γ-resonance spectroscopy [Mössbauer spectroscopy][79] that the organotin derivatives of maleic and thioglycolic acids Oct_2SnX_2, where X = OOCCH=CHCOOOct-iso or $SCH_2COOOct$-iso and Oct = octyl, mixed with PVC are converted into $Oct_2SnCl(X)$ at the end of the period T at 458 K and not into Oct_2SnCl_2, as suggested earlier by many investigators.

It is also seen from the kinetic data (Fig. 3, curve 3)[76] that at the end of the period T one acid residue in $Bu_2Sn(OOCCH{=}CHCOOC_6H_{11})_2$ is substituted by chlorine. During the first 70 min, 85% of dibutylbis(cyclohexyl maleate)tin is consumed and only 15% in the next 200 min (up to the end of the period T), i.e. almost the entire stabiliser is consumed in reactions with the active fragments present in the initial polymer.

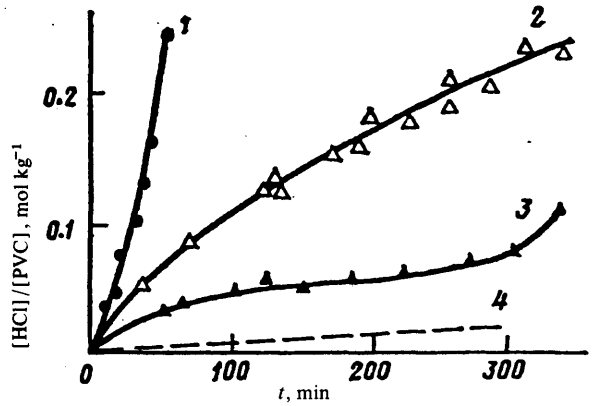


Figure 3. Kinetic curves for the dehydrochlorination of PVC at 463 K: 1) in evacuated (up to ~10^{-2} Pa) sealed tubes without the removal of volatile products; 2) *in vacuo* (~10^{-2} Pa) with constant removal of volatile products; 3) formation of ionic chlorine in the decomposition of PVC in evacuated sealed tubes containing added dibutylbis(cyclohexyl maleate)tin at a concentration of 7.0×10^{-2} mol/kg PVC; 4) theoretical curve for the dehydrochlorination of PVC in the presence of the "ideal" stabiliser.[17,76]

When the stationary section of curve 3 (Fig. 3) is extrapolated to the ordinate axis, an intercept is obtained, corresponding to the concentration of the stabiliser which has reacted with the active fragments and hence also to the concentration of the active fragments in the given PVC specimens (~2 per 1000 monomeric units).

The steady-state rate of thermal decomposition of the polymer in the presence of the stabiliser makes it possible to calculate l_{av} for the thermal decomposition of PVC *in vacuo*.[17,76] It has been established[100,101] that dialkyltin carboxylates readily undergo the exchange reaction with the chloroallyl fragments of PVC, substituting the labile chlorine atoms by groups which are more strongly bound to the polymer chains. It has been shown[11] that, after heating PVC with $Bu_2Sn(SC_{12}H_{25})_2$ or with a mixture of this compound and Bu_2SnCl_2 and the subsequent removal of the stabiliser from the polymer, the rate of thermal decomposition of PVC diminishes in proportion to the number of stabiliser fragments introduced into the PVC, which confirms the proposed[100] mechanism of the stabilisation of the polymer by organotin compounds.

Bis(alkyl maleate)dialkyltin derivatives react only slightly with the normal PVC units[76,102] and the slope of the steady-state section of curve 3 (Fig. 3) therefore corresponds to the rate of formation of dialkyltin chlorides when the stabiliser reacts with HCl and with the chloroallyl fragments arising on

decomposition of the normal units of the macrochains. Ultraviolet spectra show[17,76] that there is virtually no absorption at $\lambda > 280$ nm in the thermal decomposition of PVC in the presence of the given stabilisers, i.e. polyenes are virtually not formed and the average dehydrochlorination chain length is $l_{av}^{st} \cong 1$. Having divided the rate of formation of ionic chlorine along the steady-state section by two, it is possible to obtain the rate of dehydrochlorination of the normal PVC units for $l_{av}^{st} = 1$. Division of the steady-state rate of the thermal decomposition of PVC *in vacuo* without the stabiliser (curve *2*, steady-state section) by the rate of its decomposition in the presence of a stabiliser for $l_{av}^{st} = 1$ yields $l_{av}/l_{av}^{st} = 8$, whence $l_{av} = 8$.[17,76]

Fig. 3 also presents the theoretical curve (curve *4*) for the thermal decomposition of PVC in the presence of the "ideal" stabiliser, whereupon the dehydrochlorination of the unstable fragments is fully prevented and the decomposition of the normal unit proceeds with $l_{av}^{st} = 1$. Evidently the organotin derivatives of maleic acid approach the "ideal" polymer thermostabilisers as regards the efficiency of their action.

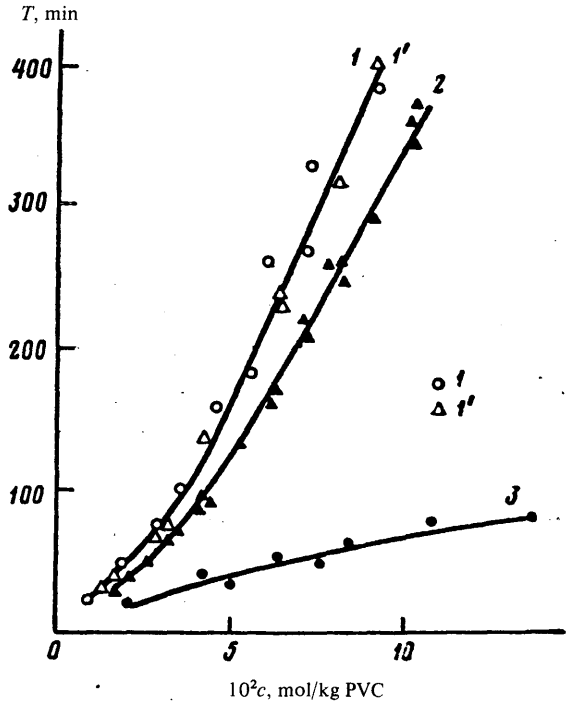


Figure 4. Dependence of the period T on the concentration of organotin maleates (c) in the thermal decomposition of PVC at 463 K: 1) dibutylbis(cyclohexyl maleate)tin; 1') bis(octyl maleate)dioctyltin; 2) dibutyltin maleate; 3) diphenyltin maleate.[76]

(b) Dependence of the Efficiency of the Stabilising Action of Organotin Compounds on Their Chemical Structure

The efficiency of the stabiliser over a wide range of concentrations can be estimated from the curves relating the period T to the concentration of the compound. It is seen from Fig. 4 that stabilisers of the type of bis(alkyl maleate)-dialkyltin derivatives are the most effective. At low stabiliser concentrations there is an inflection in the curve (curves *1* and *2*), after which the efficiency increases. The concentration of the stabiliser corresponding to the point of inflection can be called the second critical concentration. Its significance is that the rate of the bimolecular reaction of the stabiliser with unstable fragments becomes greater than the rate of decomposition of the unstable fragments from this point. The first critical concentration is that at which the rate of dehydrochlorination of the polymer diminishes in the presence of the stabiliser and the period T begins.[52,68,85]

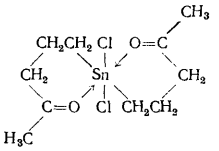
Bis(alkyl thioglycolate)dialkyltin derivatives are close in their efficiency to bis(alkyl maleate)dialkyltin derivatives, but they have one distinguishing feature, which has been noted by Troitskii et al.[76] It has been shown in model reactions[76,102] that compounds with the Sn–S bond are very reactive in nucleophilic substitution reactions with alkyl halides, which shortens the period T. The following series based on the efficiency of the stabilising effect of organotin stabilisers has been obtained from the dependence of the period T on the concentration:[17,76]

$Alk_3SnOOCCH{=}CHCOOSnAlk_3$, $Alk_2Sn(OOCCH{=}CHCOOR)_2 >$
$> Alk_2Sn(OOCCH{=}CHCOO)$, $Alk_2Sn(SCH_2COOR)_2 >$
$> Alk_3SnOOCCH{=}CHCOOR > Alk_3SnSCH_2COOR > Ph_2Sn(SCH_2COOR)_2 >$
$> AlkSn(OOCCH{=}CHCOOR)_3$, $AlkSn(SCH_2COOR)_3 > Alk_2Sn(SCH_2COO) >$
$> Ph_2Sn(OOCCH{=}CHCOO)$, $Ph_2Sn(OOCCH{=}CHCOOR)_2$ where Alk =
$=$Me, Bu, Oct; R=Et, Bu, Oct, C_6H_{11}, $-CH_2-CH_2-$,
$-CH_2-CH_2-OEt$, $-CH_2-CH_2-O-CH_2-CH_2-$.

The efficiency of the last member of the series is ten times smaller than that of the first.

In terms of the rate of interaction with s-BuCl (the low-molecular-weight model of the normal units of the PVC macrochain), organotin compounds can be arranged in a series which is the opposite of that based on the efficiency of the stabilising action.[76]

An increase in the stabilising effect is achieved when the carbonyl group is introduced into the substituent R in compounds of the type $R_2Sn(SCH_2COOR^1)_2$.[78] Thus $[CH_3C(O)CH_2CH_2CH_2]_2Sn(SCH_2COOOct)_2$ is twice as effective as the dibutyltin derivative.[78] The carbonyl group can form intramolecular complexes in dialkyltin dichlorides produced by the interaction of the stabiliser with HCl:



The catalytic activity of Alk_2SnCl_2 in such complexes is reduced.[78]

A sharp impairment of the stabilising activity of the compounds $R_2Sn(SCH_2COOR^1)_2$ is observed for R = CH_2Br or p-$CH_3OC_6H_4$, which is associated with the ease of cleavage of the Sn–C bond under the influence of HCl and the formation of a stronger catalyst of the thermal decomposition of the polymer, namely $SnCl_4$.[78]

Organotin derivatives of thioglycolic acid are more effective PVC thermal stabilisers than the derivatives of thioalcohols.[78] The authors[78] explained this by the fact that thioglycolic acid esters interact more readily with the double bonds than thioalcohols, since they give higher chain transfer rate constants. The introduction of a halogen atom (Cl, Br) into the acid residue of organotin derivatives of maleic acid diminishes the efficiency of their stabilising action.[103]

(c) The Interaction of Organotin Compounds with Low-Molecular-Weight Models of PVC

The reactions of the stabilisers of the type Bu_2SnX_2, where $X = SC_{12}H_{25}$, SCH_3, $O(O)CCH_3$, or $O(O)CC_{11}H_{23}$, with 2-chloro-2-methylbutane, 3-chlorobut-1-ene, and 1-chlorobut-2-ene have been investigated in detail.[77]

The following reactions take place in sealed tubes at 453 K;

$$RCl + Bu_2SnX_2 \rightarrow RX + Bu_2Sn(X)Cl,$$
$$2RCl + Bu_2SnX_2 \rightarrow 2RX + Bu_2SnCl_2,$$

where RCl is a chlorohydrocarbon.

Compounds with the Sn–S bond react more readily with model substances containing double bonds than with substances having a Cl atom at a tertiary carbon atom. The opposite behaviour has been observed for organotin carboxylates.[77]

It has been established[77] that the reaction of Bu_2SnX_2 with model compounds containing a double bond is accompanied by a rearrangement—a shift of the double bond. Bu_2SnCl_2 at low concentrations catalyses the rearrangement.

The interaction of the organotin compounds $RSnX_3$, R_2SnX_2, and R_3SnX, where $X = OOCCH{=}CHCOOR^1$ or SCH_2COOR^1, R = Me, Bu, Oct, or Ph, and R^1 = Et, Bu, Oct, or C_6H_{11}, with s-BuCl, which models the normal units of PVC macromolecules, at 453 K in evacuated sealed tubes has been studied.[76,102] As noted above, in terms of the rate of their interaction with s-BuCl, the compounds investigated can be arranged in a sequence which is the opposite of that based on the stabilising efficiency. In other words, the increased reactivity of the organotin compound leads to its rapid consumption in the nucleophilic substitution reaction with the normal units of the PVC macromolecules, which naturally diminishes the period T.

The reactions of organotin compounds with s-BuCl are accelerated by the products (alkyltin chlorides),[76,102] the catalytic effect diminishing in the following sequence:

$$SnCl_4 > AlkSnCl_3 > Alk_2SnCl_2 > Alk_3SnCl.$$

Thus an effective PVC stabiliser must possess the optimum reactivity towards the chlorine-containing units of the PVC macromolecules: on the one hand, it must interact vigorously with the unstable fragments of the macromolecules, and the rate of such bimolecular reaction must be higher than the rate of unimolecular thermal decomposition of the fragments, while, on the other hand, it should hardly react with the normal PVC units, since this decreases the duration of the stabilising action.

2. Synergistic Mixtures

Synergism is a phenomenon in which the stabilising action of a mixture of two or several substances exceeds the sum of the protective activities of the individual components. This phenomenon is very common in the stabilisation of polymers. The fundamental principles and mechanism of the synergistic action of binary mixtures of stabilisers in the thermo-oxidative and photo-oxidative ageing of polymers have been formulated in a book.[1]

A characteristic feature of PVC which distinguishes it from the majority of other polymers is that synergism is common in the stabilisation with respect to not only its thermo-oxidative or photo-oxidative ageing but also its thermal decomposition in the absence of oxygen. This is associated with the fact that the thermal decomposition of PVC is influenced by HCl and numerous unstable fragments of the macromolecules (Scheme 1) and that one compound cannot as a rule participate effectively in all the reactions simultaneously (certain organotin derivatives of maleic and thioglycolic acids, examined above, are an exception).

The possibilities for the combination of various compounds, each of which participates preferentially in a particular reaction (or group of reactions), are very great and numerous binary, ternary, etc. mixtures of this kind are therefore known.

Some of the products of reactions *a–h* in Scheme 1 (for example the chlorides of coordination-unsaturated metals) are, on the one hand, catalysts of reactions *b–g* (positive effects for stabilisation) and, on the other hand, they catalyse the interaction of the stabiliser with the normal units and accelerate the thermal decomposition of the polymer (negative effect). In order to attain the optimum stabilising effect, the reactivity of metal chlorides is therefore regulated by introducing complex-forming agents, which increases still further the number of synergistic mixtures.

Since reactions *a–h* take place in the polymer melt which is highly viscous, the stabiliser molecules must be capable of dissolving in PVC and diffusing in the melt. An effective stabiliser is a liquid or a readily fusible mixture of solid compounds. All additives to the stabiliser, which improve its spreading in the polymer or reduce the viscosity of the melt, increase the efficiency of the stabiliser, i.e. lead to a physical synergism.

This in fact explains the increased efficiency of the stabilising action of group IA and IIA metal carboxylates when they are introduced simultaneously with stearic acid[20] or certain polyols.[89]

(a) Mixtures Including the Chlorides of Coordination-Unsaturated Metals

The chlorides of coordination-unsaturated metals ($ZnCl_2$, $CdCl_2$, $PbCl_2$, $FeCl_2$, $FeCl_3$, $SnCl_2$, $SnCl_4$, and R_nMCl_{4-n}, where R = alkyl or aryl, M = Sn or Pb, and n = 1–3 as well as others), having low-lying unoccupied orbitals, greatly increase the stabilising activity of compounds in the first group of stabilisers (for example, organic phosphites,[20,71] epoxy-compounds,[98] organosilicon and organogermanium hydrides,[88] and oligosilanes[75]), forming synergistic mixtures with them.

The chlorides of coordination-unsaturated metals themselves exert a complex influence on the dehydrochlorination of PVC, which depends on the concentration of the additive and decomposition time. With increased concentration of the electrophilic catalyst, the initial rate of thermal decomposition of the polymer rises.[56,60,61]

The optimum concentrations of metal chlorides (which are as a rule low), at which the maximum synergistic effect is observed, have been found.[20,42,71,75,88,98]

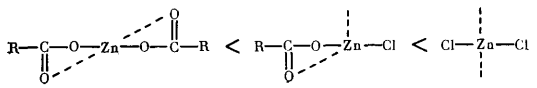
Analysis of the kinetics of the thermal decomposition of PVC in the presence of the synergistic mixtures considered, as well as the study of reactions with model compounds,[42,71,75,88,98,99,102,104] make it possible to conclude that the metal chlorides catalyse the interaction of the stabilisers in the first group with the unstable fragments of the macromolecules and with the double and conjugated double bonds (Scheme 1, reactions *b–f*).

Metal chlorides which do not behave as Lewis acids do not form synergistic mixtures of this kind.[42,71,75,88]

(b) Mixture of Other Compounds of Coordination-Unsaturated Metals with Organic Stabilisers

Synergistic mixtures with organic stabilisers (organic phosphites, epoxy-compounds, aminocrotonic acid esters, oligosilanes) are also formed by the carboxylates of coordination-unsaturated metals (zinc, cadmium, and dialkyltin),[20,34,42,69,71,75,99] organotin compounds (Ph_4Sn, trialkyl- and triaryltin isocyanates, and others),[20,86] and organolead compounds (Ph_4Pb and triphenyl-lead isocyanate).[87] The carboxylates of alkali and alkaline earth metals do not form synergistic mixtures with organic stabilisers.[20,34,42,69-71]

Mixtures of the above compounds of coordination-unsaturated metals with organic stabilisers are more effective than the mixtures with the corresponding metal chlorides[20,34,42,69,71,75] apparently because these compounds themselves stabilise PVC. Furthermore, as a result of the interaction of the metal compounds with HCl and with the unstable fragments, mixed chlorides are formed which are weaker catalysts of the thermal decomposition of the polymer than the metal chlorides. For example, the zinc salts can be arranged in the following sequence in terms of their catalytic activities:



Thus the reactivity of the zinc salt as a catalyst increases as the coordination sphere of the metal is opened.

(c) Mixtures of Zn–Ca and Cd–Ba Carboxylates

The mechanism of the synergistic action of a mixture of zinc and calcium carboxylates has been investigated.[89,99,105] As a consequence of the exchange reaction between the calcium carboxylate and $ZnCl_2$, a powerful catalyst of the dehydrochlorination of PVC is removed and zinc carboxylate, which readily enters into a nucleophilic substitution reaction with the unstable fragments of the macromolecules, is reformed.[99,105]

Calcium and zinc carboxylates form complexes with one another[99,105] and with zinc and calcium chlorides (mixed complexes).[99] The catalytic activity of $ZnCl_2$ in these complexes is reduced.[99]

Zinc carboxylates react also with the normal units of PVC, accelerating their decomposition, while calcium carboxylates diminish the rate of this reaction probably because the salts form complexes with one another.[89]

A study of the thermal decomposition of PVC in the presence of a synergistic mixture of cadmium and barium carboxylates established[70] that initially mainly $CdCl_2$ is formed (up to 90%), although the starting amounts of barium and cadmium carboxylates were identical. In the presence of barium stearate, cadmium chloride does not accelerate the decomposition of PVC, which suggests the formation of a complex between $CdCl_2$ and the barium salt.[70]

It was shown above that the synergistic effect is observed when individual stabilisers of the first and third groups are employed jointly. We shall consider synergistic mixtures in which the second component is not a stabiliser.

(d) Mixtures of Carboxylates of Coordination-Unsaturated Metals with Compounds Containing the OH, SH, and NH Groups

Mixtures of polyols with the carboxylates of coordination-unsaturated metals (Group IIB, III, and IV metals) exhibit an appreciable synergistic effect on the processes occurring in the thermal decomposition of PVC.[89-96] In their presence the rate of dehydrochlorination falls during the period T to the rate of decomposition of PVC *in vacuo*, an appreciably smaller insoluble fraction is produced, and the polymer does not become coloured.[89-91] As an example, Fig. 5 presents the dependence of the period T on the concentration of polyols in the presence of zinc and cadmium stearates.

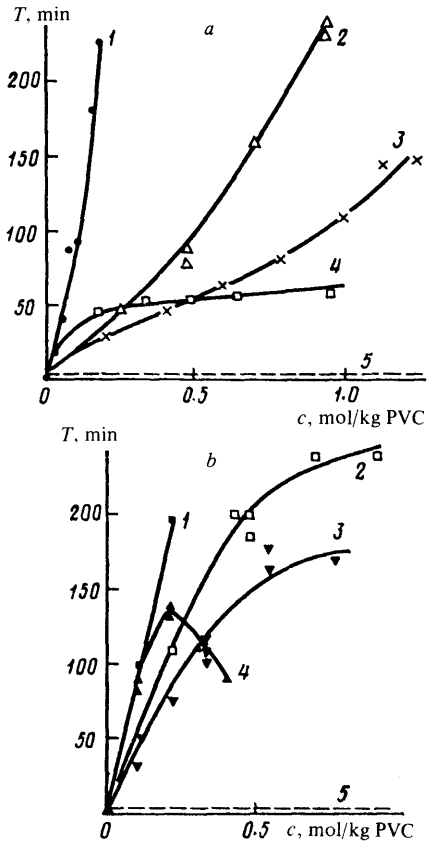
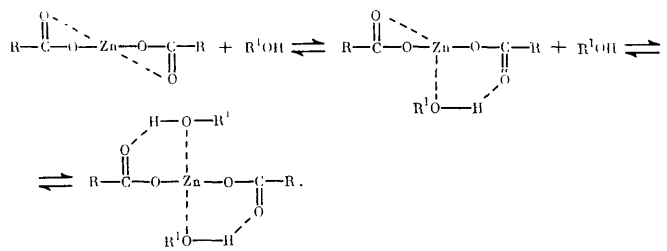


Figure 5. Dependence of the period T on the concentration of polyols in the thermal decomposition of PVC at 453 K in the presence of zinc stearate at a concentration of 0.1 mol/kg PVC (*a*) or cadmium stearate at a concentration of 0.05 mol/kg PVC (*b*).[89] *a*: 1) pentaerythritol; 2) ethylene glycol; 3) stearyl alcohol; 4) triethylene glycol; *b*: 1) glycerol; 2) ethylene glycol; 3) octyl alcohol; 4) triethylene glycol; the dashed lines represent the theoretical curves plotted assuming the additivity of the effects of the mixture components (curves 5).

The efficiency of the synergistic action of the mixtures diminishes in the following sequence: polyols > triols > diols > aliphatic alcohols; zinc carboxylate > cadmium carboxylate > tin(II) carboxylates > aluminium carboxylate.

The following observations have been made as regards the effect of mixtures of polyols with zinc and cadmium carboxylates on the thermal decomposition of s-BuCl, a low-molecular-weight compound modelling the normal fragments of the polymer:[89-91] (1) the polyols greatly reduce the rate of reaction of the carboxylates of coordination-unsaturated metals with the normal PVC unit; (2) the thermal decomposition of PVC in the presence of a mixture of carboxylates of these metals with polyols involves the exchange of a chlorine atom in the chlorine-containing groups of the polymer not only for the carboxy-group of the salt but also for the alcoholic residue; (3) salts of coordination-unsaturated metals also catalyse the addition of polyols to the double (conjugated double) bonds; (4) the polyols inhibit the catalytic effect of the chlorides of coordination-unsaturated metals on the thermal decomposition of PVC and s-BuCl; (5) among the large number of oxygen-, sulphur-, and nitrogen-containing compounds capable of forming donor–acceptor complexes of the *nV* type with zinc salts, only those containing the OH, SH, and NH groups respectively give rise to effective synergistic mixtures with zinc carboxylates.

The results can be explained by the fact that the carboxylates of coordination-unsaturated metals and compounds with the OH, SH, and NH groups form complexes having a cyclic structure (resembling chelates):



It is known that chelate complexes have a higher thermal stability and are chemically more reactive than complexes with a non-chelate structure.[106]

The formation of six-membered cyclic complexes between the carboxylates of coordination-unsaturated metals and polyols results in a considerable decrease of the rates of reaction of metal carboxylates with the normal units of the macromolecules.[89-91] At the same time, the complexes retain a high reactivity towards the active unstable fragments of the macrochains (Scheme 1, reactions *b*–*f*).

A definite contribution to the synergism of the action of the coordination-unsaturated metal carboxylate–polyol mixtures comes also from the formation of complexes by the polyols with the chlorides of the same metals.[81,89-96]

Group I and IIA metal carboxylates do not form complexes with *n*-electron donors and do not give rise to mixtures with polyols exhibiting a synergistic activity like the mixtures of polyols with coordination-unsaturated metal carboxylates.[89-96]

Certain polyols, for example diethylene and triethylene glycols give rise to an antagonistic effect with the carboxylates of Group I and IIA metals (Li, Na, Mg, Ca, Sr, and Ba). These polyols can probably act like crown-ethers, shielding the cations and enhancing the nucleophilicity of the anion, which accelerates the decomposition of PVC via the anionic mechanism:[89]

$$CaSt_2 + n\text{TEG} \rightarrow St^-[Ca - - - n\text{TEG}]^{2+}St^-,$$

where TEG = triethylene glycol and St = stearic acid residue.

Ternary mixtures, for example, zinc carboxylate–calcium carboxylate–polyol and cadmium carboxylate–barium carboxylate–polyol, exhibit a still greater synergistic effect than the binary mixtures of components (Fig.6).[89] In their presence the rate of accumulation of ionic chlorine is lower than in the decomposition of the polymer without additives *in vacuo*. In the ternary mixture the catalytic activity of zinc salts in relation to the normal units of PVC is reduced still further compared with the binary mixtures, which has been demonstrated by model reactions with s-BuCl.[89]

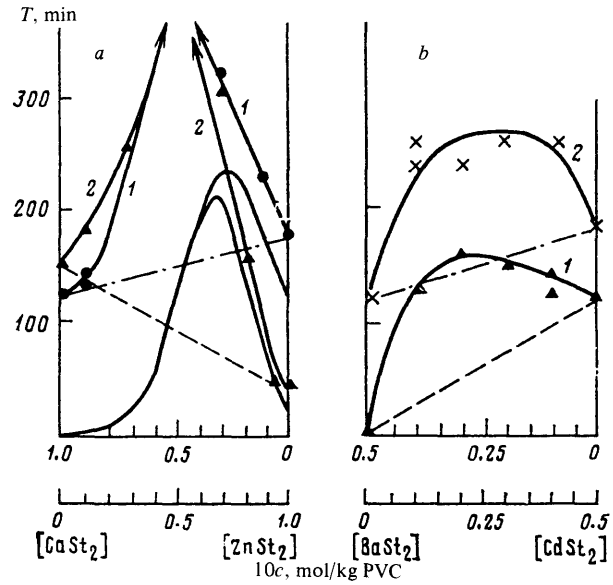


Figure 6. Dependence of the period *T* on the calcium stearate/zinc stearate (*a*) or barium stearate/cadmium stearate (*b*) molar ratio in the thermal decomposition of PVC at 453 K in the presence of polyols (mol/kg PVC):[89]
a: 1) 0.15 pentaerythritol; 2) 0.23 ethylene glycol;
b: 1) 0.1 stearyl alcohol; 2) 0.56 octyl alcohol; the dashed lines represent the theoretical curves plotted assuming the additivity of the effects of the mixture components; the thin continuous lines without symbols represent the limits of the region in which the white colour of PVC is retained.

3. Characteristic Features of the Reactions between the Stabiliser and PVC

We shall now consider the characteristics of the reactions between the stabiliser and the unstable fragments—the double (conjugated double) bonds in PVC.[107]

1. Compounds of coordination-unsaturated metals (Sn, Pb, Zn, Cd, Sb, etc.) participate in nucleophilic substitution reactions of the unstable fragments of PVC macromolecules. Compounds of these metals enter into the composition of the most effective PVC thermostabilisers.

2. The PVC melt (433–473 K) containing the added stabiliser is a dielectric with a low electrical conductivity and the formation of ions in such a system is unlikely. In terms of the classification of nucleophilic substitution reactions adopted in organic chemistry[8] the reactions of PVC with the stabiliser can be classified as belonging to the class of S_N2 bimolecular nuclophilic substitution reactions, subject to the stipulation that the reaction proceeds not between the anion and an alkyl chloride but apparently in a complex of the CTC

type, where the donor is the polymer fragment and the acceptor is the compound of the coordination-unsaturated metal.

3. It has been shown on model compounds that fragments containing chlorine in the allyl position and at the branching points are much more reactive in nuclophilic substitution reactions than the normal chain units. The large difference between the rates of these reactions makes it possible to select a compound of the coordination-unsaturated metal such that at 443–473 K it hardly interacts with the normal PVC units but reacts rapidly with the labile groups. All the effective PVC stabilisers satisfy this condition.

4. The nuclophilic substitution reaction is complicated by the elimination of HCl. The rate of the elimination reaction is determined by the electrophilic properties of both the initial components of the stabiliser and those of the products of their interaction with HCl and the chlorine-containing PVC fragments. Coordination-unsaturated metal chlorides accelerate the reaction of the stabiliser with the chlorine-containing fragments and the HCl elimination reaction.

5. Complex-forming agents containing O, S, N, and P atoms and forming complexes with compounds of coordination-unsaturated metals influence the rates of nucleophilic substitution and HCl elimination reactions. The best stabilising effects are attained when compounds having several OH, SH, and NH groups are used.

6. The rate of reaction between the stabiliser and PVC is lower than the rate of its reaction with the low-molecular-weight model compound, which apparently can be accounted for by the high viscosity of the polymer melt and the complication of the process by diffusion phenomena.

7. Whereas the nucleophilic substitution reactions are being vigorously investigated and they explain the mechanism of action of the majority of stabilisers, the reactions of the stabilisers with double and conjugated double bonds have been inadequately studied. At the same time, polyenes exhibit an increased reactivity at elevated temperatures (440–480 K): they participate in intramolecular and intermolecular reactions with liberation of benzene and the formation of a cross-linked polymer. The catalytic action of HCl is associated with its reversible addition to polyenes (reactive intermediate species, namely the ion pairs formed in this reaction, accelerate the thermal decomposition of PVC).

The steric structure of the polyenes should play a major role: dienophiles should interact only with *cis*-dienes, benzene can be formed only in the presence of triads of conjugated double bonds with a specific steric structure, etc.

The increased stabilising effect of many synergistic mixtures of compounds of coordination-unsaturated metals with substances containing the OH, SH, and NH groups as well as other organic compounds is associated with the increase in the rates of reactions involving electrophilic addition to double and conjugated double bonds.

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