Some Aspects of the Thermal Degradation of Poly(Vinyl Chloride)

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The kinetic perculiarities and mechanism of the nonautocatalytic thermal degradation of PVC with effective removal of HCl are discussed. The papers which are concerned with the mathematical models of the initial stage of the nonautocatalytic thermal dehydrochlorination of idealized PVC, i.e., PVC having no abnormal fragments, the polymer, containing VC units and abnormal groups and the polymer having macromolecules with various stereoregularity, are considered. Mechanism of the autocatalytic thermal degradation of PVC in the presence of HCl is discussed.

Keywords: PVC; thermal degradation; dehydrochlorination; autocatalytic; mathematical models

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most important commercial polymers. But PVC still poses many problems. Its rather low stability to the influence of heat and light requires stabilization of the polymer for practically all technical applications.

The thermal degradation of PVC begins at temperatures above 100°C. PVC is one of the polymers, which decompose with isolation of side fragments from macromolecules. This leads to formation of HCl (> 90%) and polyenes:

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$$\sim(CH_2 \text{---} CHCl)_n \sim \rightarrow mHCl + \sim(CH_2 \text{---} CHCl)_{n-m} - (CH \text{==} CH)_m \sim$$

$$(1)$$
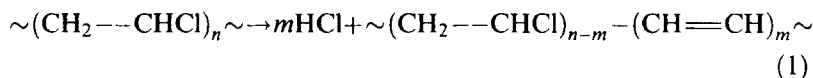
where $n > m$.

In spite of apparent simplicity of this summary reaction (1) the mechanism of the thermal degradation of PVC is very complicate. Besides units of vinyl chloride (VC) PVC macromolecules have abnormal fragments which appear due to peculiarities of radical polymerization of VC. At elevated temperatures polyenes, which form in the thermal degradation of PVC, may take part in the secondary reactions with each other, with HCl and so on. The thermal degradation of PVC is complicated by the catalytic effect of evolving HCl.

Effort to solve the degradation problems have led to the performance of many researches beginning with the papers cited in [1 – 3]. In recent years, the mechanism of the thermal degradation of PVC is intensively studied [4 - 14].

It is well known [3 – 14] that the initial rate of the nonautocatalytic degradation of PVC with effective removal of HCl is much more than that of chlorohydrocarbons which are the low molecular weight models of the normal units of the polymer. It is generally assumed that structural abnormalities in the PVC chains are mainly responsible for the low thermal stability of the polymer [3 – 14]. There is considerable discussion about the nature and concentration of unstable fragments of PVC macromolecules and about their influence on the initial stage of polymer degradation [3 – 14]. The most important reason behind this is the difficulty in identifying and quantifying of the structural irregularities. The level of these abnormalities in the polymer is extremely low.

It has been shown that PVC contains 0.1–0.5 mol% of double bonds, 0.01 – 0.05 mol% of the internal chloroallytic fragments, 0.1 – 0.3 mol% of branching groups having the chlorine atom near the tertiary carbon atom, ~ 0.01 mol% of peroxide and hydroperoxide groups, up to 0.02 mol% of the internal "head-to-head" structures [3 – 14]. The authors of the paper [9] assume all the internal chloroallylic fragments to be conjugated ketoallylic groups.

Studies of the thermal degradation of the low molecular weight chlorohydrocarbons have shown that the internal chloroallytic structures, fragments with the chlorine atom near the tertiary carbon

atom are unstable groups of PVC macromolecules [3 – 15]. Marcomo-dels of PVC, containing known amounts of different unstable groups, have also been investigated. It has been demonstrated that an increase in concentration of the internal chloroallylic fragments, branching groups having the chlorine atom near the tertiary carbon atom, peroxide and hydroperoxide fragments leads to considerable increase of the initial rate of the thermal degradation of PVC [4 – 14].

On the other hand, it is proposed that tacticity of macromolecules are mainly responsible for the low thermal stability of PVC [5, 12, 13].

It is assumed [16 – 25] that one of the reason of the low thermal stability of PVC in comparison with the low molecular weight models of the normal units of the polymer is that PVC macromolecules contain much longer chains of VC units than investigated chlorohy-drocarbons. The thermal degradation of low molecular weight model chlorohydrocarbons having only 1 – 2 units of VC has been studied in the liquid phase [14, 15].

The present review is concerned with several aspects of the thermal dehydrochlorination of PVC which have been studied recently by the authors and their collegues. Most of this work has been directed towards a detailed understanding of the kinetic peculiarities and mechanism of the nonautocatalytic degradation of PVC with effective removal of HCl and it has been greatly assisted by the use of the method of the mathematical models. In this review the mathematical models of the initial stage of the nonautocatalytic thermal degradation of idealized PVC, *i.e.*, PVC having no abnormal fragments, the poly-mer which contains VC units and abnormal groups and the polymer having macromolecules with various stereoregularity, are considered.

Mechanism of the autocatalytic thermal degradation of PVC in the presence of HCl is discussed.

1. KINETIC PECULIARITIES OF THE INITIAL STAGE OF THE NONAUTOCATALYTIC THERMAL DEGRADATION OF PVC WITH EFFECTIVE REMOVAL OF HCL

It is known [4 – 14] that in the presence of volatile products the thermal dehydrochlorination of PVC has an autocatalytic character, connected with the accelerating effect of HCl. The thermal degradation of PVC

proceeds at different concentrations of HCl in the polymer depending on conditions in which experiment is carried out. In the paper [25] it has been discussed two extreme cases between which one can place many intermediate versions of the thermal degradation of PVC:

(i) A thin layer of twice precipitated PVC is decomposed in high vacuo with continuous

and effective removal of HCl or a dilute solution of PVC in inert solvent is degraded

with continuous and effective removal of HCl by stream of inert gas.

(ii) PVC is degraded in closed reaction vessel. HCl is not removed.

In the first case, dehydrochlorination rate has maximum value at the beginning and then decreases during the early stage and become principally steady up to some percent of conversion (Fig. 1, Curve 1) [10, 11, 16, 17, 21, 24–43]. In the second case, the kinetic curves of PVC dehydrochlorination have an autocatalytic character [10, 25, 27, 29, 32, 33, 35–37].
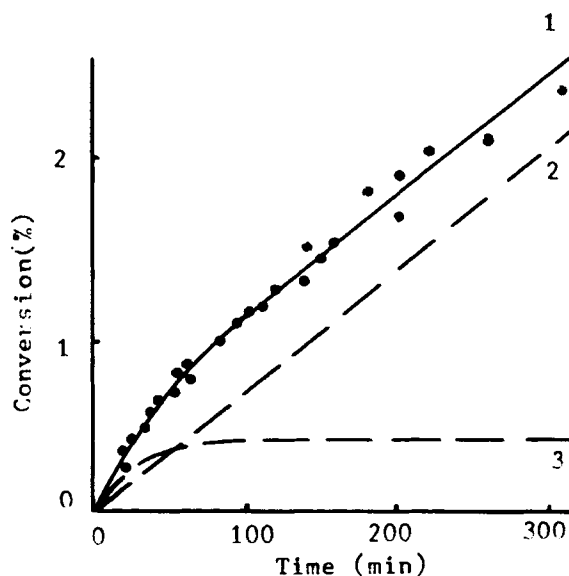

FIGURE 1   Kinetic curve of dehydrochlorination of PVC in vacuo ($\sim 10^{-4}$ mm Hg) with continuous removal of HCl by freezing at 200°C (1), separated into curves 2 and 3 [29].

In the papers [38, 39] critical phenomena which are observed in the thermal degradation of the polymer with continuous and effective removal of HCl, has been investigated. It has been obtained the value of critical thickness of PVC film, *i.e.*, maximum thickness of the polymer film at which the thermal degradation of the polymer with effective removal of volatile products proceeds without autocatalysis. It is equal to 0.24, 0.18 and 0.15 mm at 190, 200 and 210°C respectively [39].

The influence of reprecipitation of PVC samples on the thermal degradation of the polymer with effective removal of HCl has been discussed [25].

Sections 1 – 4 of this review deals with the first case of the thermal degradation of PVC with continuous and effective removal of HCl. In Section 5 the mechanism of the autocatalytic thermal degradation of PVC in the presence of HCl is considered.

It has been shown [29, 36, 37, 40, 41, 43] that the kinetic curves of the initial stage (upto 10% conversion) of the nonautocatalytic thermal dehydrochlorination of PVC with effective removal of HCl at 180 – 210°C (Fig. 1, curve 1) may be separated into two curves (curves 2 and 3) which are described by the equations for first-order reactions with different rate constants. The supposition has been made that the overall process of PVC dehydrochlorination consists of two processes which proceed simultaneously [10, 29, 36, 37, 40, 41, 43]. It has been proposed that curve 3 corresponds to the thermal dehydrochlorination of unstable fragments, present in the original polymer, and curve 2 corresponds to the thermal degradation of PVC initiated by dehydrochlorination of the normal units of macromolecules (Fig. 1). As can be seen from Figure 1 (curve 3), unstable fragments, present in the original polymer, degrade completely during the early stage of PVC dehydrochlorination (less than 2% conversion). From the half-conversion period, $\tau_{1/2}$, (Fig. 1, curve 3) the effective constants of rates of degradation of unstable fragments, k^{ef}_{unstab}, has been calculated for various samples of PVC [36, 37, 40, 41, 44] (Tab. I). For the sample B (Tab. I) the thermal degradation of unstable fragments, present in the original polymer, has been described by the equation for first-order reaction with the following effective rate constant [29, 36, 37, 40, 43]:

$$k^{ef}_{unstab} = 10^{9.6\pm0.5} \times e^{-28000\pm1000/RT} \ \sec^{-1} \qquad (2)$$

Above ~2–3% conversion the thermal degradation of PVC is initiated by the statistic degradation of the normal units of the polymer (Fig. 1) [10, 29, 36, 37, 40, 41, 43].

In the papers [29, 40, 41]the thermal degradation of PVC has been carried out at higher temperatures, *viz.*, 220–250°C and upto more percent of conversion, *viz.*, 25–70%. The kinetic curves for PVC degradation at 220–250°C are described by the equation for first-order reaction up to ~40% conversion. Above ~40% conversion the rate of PVC dehydrochlorination decreases more considerably than that calculated from the equation for first-order reaction.

The following Arrhenius expression for the effective constant of the rate of the thermal dehydrochlorination of PVC initiated by the statistic degradation of the normal units of the polymer, k_0^{ef}, has been obtained from the dependence of the logarithm of the initial rate of this reaction on $1/T$ at 180–250°C [29, 40, 41]:

$$k_0^{ef} = 10^{11.8 \pm 0.5} \times e^{-38000 \pm 1000/RT} \ sec^{-1} \qquad (3)$$

It is shown [29, 43] that

$$k_0^{ef} = k_0 \, l_{av} \quad \text{and} \quad k_0 = k_0^{ef}/l_{av} \qquad (4)$$

where k_0 is the constant of the rate of the thermal degradation of the normal units of PVC; l_{av} represents the average length of kinetic chain of PVC dehydrochlorination. The value of l_{av} has been determined to be equal to 8–15 [28–30, 45].

TABLE I   The values of the effective rate constants of the thermal degradation of unstable fragments of various samples of PVC, k_{unstab}^{ef}, at 200°C calculated in [44] by method from [36, 37, 40, 41]

Number	Sample of PVC	$k_{unstab}^{ef} \times 10^4, \ sec^{-1}$
1.	A	4.44
2.	B	6.24
3.	C	2.96
4.	D	3.6
5.	H	2.31
6.	K	2.31

Note: A, B, C and D are samples from Ref. [25]; H and K are samples from Ref. [28].

From the Eqs. (3) and (4) at $l_{av} = 8$ [29, 30] the following expression for k_0 has been obtained [43]:

$$k_0 = 10^{11.0 \pm 0.5} \times e^{-38000 \pm 1000/RT} \ \sec^{-1} \qquad (5)$$

2. MATHEMATICAL MODELS OF THE INITIAL STAGE OF THE THERMAL DEGRADATION OF PVC OBTAINED BY THE USE OF THE THEORY OF PROBABILITY AND THE THEORY OF THE CONSECUTIVE REACTIONS

In the papers [16–24] the mathematical models of the initial stage (upto 10% conversion) of the thermal dehydrochlorination of PVC has been proposed using the theory of probability and the theory of the consecutive reactions [46] by means of consideration of the degradation of the low molecular weight models for various fragments of PVC macromolecules by molecular mechanism in inert atmosphere in the absence of catalytic effect of HCl without consideration of perculiarities of stereochemical structure of model chlorohydrocarbons at the assumption that $k_0 \ll k_1 \ll k_2 \cong k_3 \cong \ldots \cong k_{n-1}$, where k_1, $k_2, \ldots, k_{n-1}$ represent the effective constants of rates of dehydrochlorination of fragments with $1, 2, 3, \ldots, n-1$ double bonds respectively; n is the number of VC units in chlorohydrocarbon. It has been used the values of k_0, k_1 and k_2 which have been obtained in the thermal degradation of chlorohydrocarbons in the liquid phase in the absence of HCl [15].

2.1. The Thermal Degradation of Low Molecular Weight Chlorohydrocarbons Containing only VC Units

It has been shown [18, 23, 24] that the initial stage of the thermal degradation of model chlorohydrocarbons containing only VC units and having "head-to tail" structure may be described by the following expressions:

$$[HCl]_{norm} = l_{av} C_0^0 (1 - e^{-k_0 t}) - (l_{av} - 1) - C_0^0 \frac{k_0}{k_1} (1 - e^{-k_1 t}) \qquad (6)$$

$$V_{norm} - [l_{av}k_0e^{-k_0t} - (l_{av} - l)k_0e^{-k_1t}]C_0^0 \qquad (7)$$

where C_0^0 represents the initial concentration of chlorohydrocarbon; t is the time of degradation.

In statistic initiation l_{av} may be defined as [23]:

$$l_{av} = \sum_{i=1}^{n} \frac{l_i}{n} = \frac{1}{2}(n+1) \qquad (8)$$

Figure 2 shows the calculated from the Eq. (7) curves of the dependence of the dehydrochlorination rate on time for degradation of chlorohydrocarbons having different number of VC units at 200°C
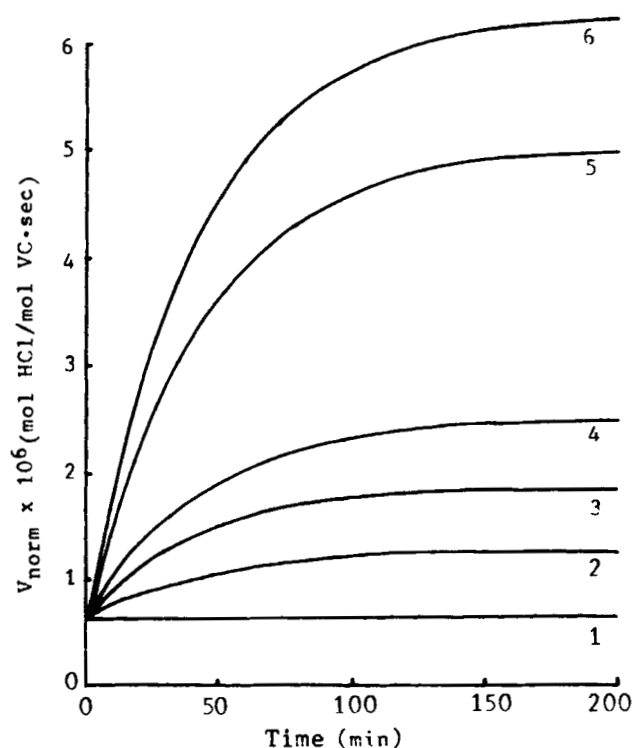

FIGURE 2   Calculated from Eq. (7) curves of the dependence of dehydrochlorination rate on time for the thermal degradation of chlorohydrocarbons, having different number of VC units (n), at 200°C: (1) $n = 1$; (2) $n = 3$; (3) $n = 5$; (4) $n = 7$; (5) $n = 15$; (6) $n = 19$ [18].

[18]. It is seen that the rates of degradation of compounds with $n \geq 2$ increases in the early stage and then become practically steady. In the stationary part of dehydrochlorination curves the rate of degradation, V_{stat}, may be described by the following equation which is typical for unbranching chain reactions [23, 24]:

$$V_{stat} = V_{init}l_{av} = k_0 C_0 l_{av} \qquad (9)$$

where V_{init} is the rate of initiation.

As can be seen from the Eqs. (6)–(9) and Figure 2, the value of l_{av} is of particular importance in the initial stage of the thermal degradation of chlorohydrocarbons. The less is the number of VC units in chlorohydrocarbon, the more stable it is.
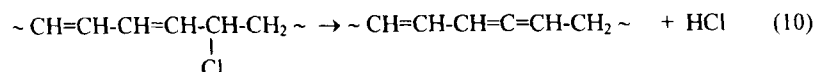
It has been shown [18, 23, 24] that the Eqs. (6) and (7) may be used for the initial stage of the thermal degradation of idealized PVC if the values of l_{av} for the thermal dehydrochlorination of PVC and the model compounds are equal to each other.

In the paper [23] the possible reactions of termination of chain of the thermal dehydrochlorination of chlorohydrocarbons, such as intermolecular Diels-Alder reaction between generated polyenes and the reaction of intramolecular cyclization of formed trienes and tetraenes, have been examine. The rates of reactions of chain termination have been compared with the rate of dehydrochlorination quantitatively [23].

It has been shown that the termination of dehydrochlorination chain of chlorohydrocarbons occurs most probably due to the reaction of intramolecular cyclization of generated tetraenes and that in the thermal degradation of chlorohydrocarbons having $n \geq 7$, $l_{av} \geq 4$.

As mentioned above in the thermal degradation of PVC the value of l_{av} has been determined to be equal to $8 - 15$ [28 – 30, 45]. Substitution of these values of l_{av} into the Eq. (8) shows that low molecular weight chlorohydrocarbons, which may serve as models for PVC macromolecules, must contain 15 units ot VC at the minimum. Except the reaction of intramolecular cyclization of tetraenes there are other reactions which may lead to the termination of dehydrochlorination of chlorohydrocarbons. The termination of dehydrochlorination chain may take place due to stereochemical reasons when there is no conjugation of forming double bond with before generated conjugated

double bonds [27]. The termination of chain may result from the reaction of formation of allene fragments by the following equation too:

$$\sim CH=CH\text{-}CH=CH\text{-}\underset{\underset{Cl}{|}}{CH}\text{-}CH_2 \sim \; \rightarrow \sim CH=CH\text{-}CH=C=CH\text{-}CH_2 \sim \;\; + \; HCl \qquad (10)$$

2.2. The Thermal Degradation of Low Molecular Weight Hydrocarbons Containing VC Units and Unstable Fragments
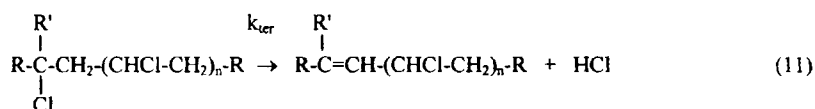
The mathematical models of the thermal degradation of these model compounds have been considered under the following additional conditions [17, 21, 24]:

(i) The reaction of initiation, *i.e.*, elimination of the first molecule of HCl, occurs from the untstable fragment always.

(ii) The termination of dehydrochlorination chain occurs due to the reaction of intramolecular cyclization of generated tetraenes.

2.2.1. The Thermal Degradation of Low Molecular Weight Chlorohydrocarbons Having VC Units and Branching Fragments with the Chlorine Atom Near the Tertiary Carbon Atom

The thermal degradation of these chlorohydrocarbons may be described by the following equations:

Initiation:

$$R\text{-}\underset{\underset{Cl}{|}}{\overset{\overset{R'}{|}}{C}}\text{-}CH_2\text{-}(CHCl\text{-}CH_2)_n\text{-}R \;\; \overset{k_{ter}}{\rightarrow} \;\; R\text{-}\overset{\overset{R'}{|}}{C}=CH\text{-}(CHCl\text{-}CH_2)_n\text{-}R \;\; + \;\; HCl \qquad (11)$$

Propagation:

$$R\text{-}\overset{\overset{R'}{|}}{C}=CH\text{-}(CHCl\text{-}CH_2)_n\text{-}R \;\; \overset{k_1'}{\rightarrow} \;\; R\text{-}\overset{\overset{R'}{|}}{C}=CH\text{-}CH=CH\text{-}(CHCl\text{-}CH_2)_{n\text{-}1}\text{-}R \;\; + \;\; HCl \qquad (12)$$

Termination:

$$\underset{\mathrm{R\text{-}C=CH\text{-}(CH=CH)_{lav-5}\text{-}(CH=CH)_4\text{-}(CHCl\text{-}CH_2)_{n\text{-}lav+1}\text{-}R}}{\overset{\mathrm{R'}}{\underset{|}{}}} \quad \overset{k_t}{\longrightarrow}$$

$$\longrightarrow \quad \begin{array}{c} \mathrm{R'} \\ | \\ \mathrm{R\text{-}C=CH\text{-}(CH=CH)_{lav-5}\text{-}CH} \\ | \\ \mathrm{R\text{-}(CHCl\text{-}CH_2)_{n\text{-}lav+1}\text{-}CH} \\ \diagdown \\ \end{array} \begin{array}{c} \mathrm{CH=CH} \\ \diagup \quad \diagdown \\ \mathrm{CH} \\ \| \\ \mathrm{CH} \\ \diagup \\ \mathrm{CH=CH} \end{array} \qquad (13)$$
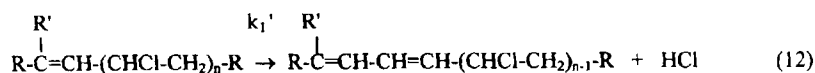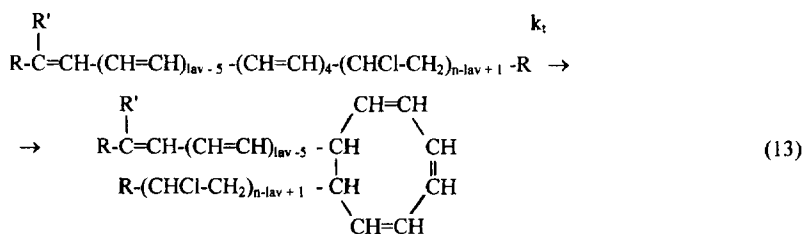
where R is alkyl; k_{ter} represents the effective constant of rate of dehydrochlorination of branching fragments with the chlorine atom near the teritary carbon atom; k_t is the constant of the rate of termination of dehydrochlorination chain.

The following expressions for the initial stage of degradation of model chlorohydrocarbons containing VC units and fragments with the chlorine atom near the tertiary carbon atom have been deduced [21, 24]:

$$V_{\text{ter}} = k_{\text{ter}} C_{\text{ter}}^0 \left[e^{-k_{\text{ter}}t} + (l_{\text{av}} - 1) \frac{k_1'}{k_{\text{ter}} - k_1'} (e^{-k_1't} - e^{-k_{\text{ter}}t}) \right] \qquad (14)$$

$$[\mathrm{HCl}]_{\text{ter}} = C_{\text{ter}}^0 (1 - e^{-k_{\text{ter}}t}) - (l_{\text{av}} - 1) C_{\text{ter}}^0 \frac{k_1'}{k_{\text{ter}} - k_1'} (1 - e^{-k_{\text{ter}}t}) + (l_{\text{av}} - 1) C_{\text{ter}}^0$$

$$\times \frac{k_{\text{ter}}}{k_{\text{ter}} - k_1'} (1 - e^{-k_1't}) \qquad (15)$$

where C_{ter}^0 represents the initial concentration of chlorohydrocarbon having fragment with the chlorine atom near the tertiary carbon atom.

Figure 3 shows calculated from Eq. (14) curves of the dependence of rate on time for the thermal degradation of these chlorohydrocarbons at 200°C. It has been used the value of k_{ter} which was obtained for the thermal degradation of low molecular weight chlorohydrocarbon in the liquid phase in the paper [47]. As can be seen from Figure 3, the dependences of rate of dehydrochlorination of chlorohydrocarbons on time have maximum at short times of degradation. The greater l_{av} and C_{ter}^0, the more considerble maximum becomes. Then the dehydrochlorination rate decreases up to small value. Figure 3 demonstrates that low molecular weight model chlorohydrocarbons having branching fragments with the chlorine atom near the tertiary carbon atom degrade completely for $\sim 200\,\mathrm{min}$ at 200°C.
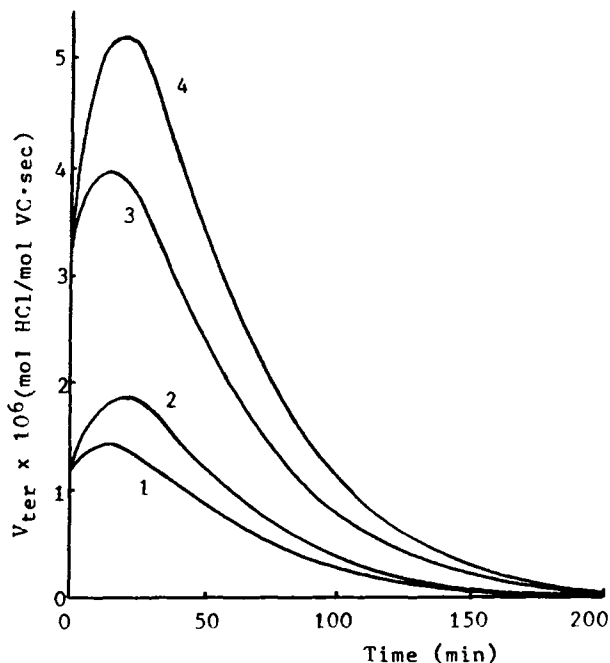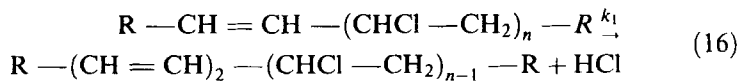
FIGURE 3   Calculated from Eq. (14) curves of the dependence of dehydrochlorination rate on time for the thermal degradation of chlorohydrocarbons, having VC units and fragment with the chlorine atom near the tertiary carbon atom, at different l_{av} and C_{ter}^0 at 200°C in inert solvent: (1) and (3) $l_{av} = 6$; (2) and (4) $l_{av} = 8$; (1) and (2) $C_{ter}^0 = 0.1$ mol% (3) and (4) $C_{ter}^0 0.28$ mol% [21].

2.2.2. The Thermal Degradation of Low Molecular Weight Chlorohydrocarbons Having VC Links and the Internal Chloroallylic Fragments

The thermal degradation of these chlorohydrocarbons may be represented by the following equations:

Initiation:

$$R-CH = CH-(CHCl-CH_2)_n-R \xrightarrow{k_1}$$
$$R-(CH = CH)_2-(CHCl-CH_2)_{n-1}-R + HCl \tag{16}$$

Propagation:

$$R-(CH = CH)_2-(CHCl-CH_2)_{n-1}-R \xrightarrow{k_2}$$
$$R-(CH = CH)_3-(CHCl-CH_2)_{n-2}-R + HCl \tag{17}$$

Termination:

$$k_t$$

$$R\text{-}(CH=CH)_{lav\text{-}3}\text{-}(CH=CH)_4\text{-}(CHCl\text{-}CH_2)_{n\text{-}lav}\text{-}R \rightarrow$$

$$\begin{array}{c} CH=CH \\ \diagup \qquad \diagdown \\ \rightarrow \quad R\text{-}(CH=CH)_{lav\text{-}3}\text{-}CH \qquad CH \\ \mid \qquad \qquad \mid \\ R\text{-}(CHCl\text{-}CH_2)_{n\text{-}lav}\text{-}CH \qquad CH \\ \diagdown \qquad \diagup \\ CH=CH \end{array} \qquad (18)$$

It has been shown that the initial stage of the thermal degradation of these model chlorohydrocarbons may be described by the following expressions [21, 24]:

$$V_{all} = k_1 C_{all}^0 e^{-k_1 t} l_{av} \qquad (19)$$

$$[HCl]_{all} = C_{all}^0 (1 - e^{-k_1 t}) l_{av} \qquad (20)$$

where C_{all}^0 represents the initial concentration of chlorohydrocarbon containing the internal chloroallylic fragment.

Figure 4 shows calculated from Eq. (19) curves of the dependence of rate on time for the thermal degradation of these chlorohydrocarbons at 200°C. As can be seen the initial rate of degradation of chlorohydrocarbons is in direct proportion to concentration of chloroallylic fragments and l_{av}. The time of full degradation of model compound containing the chloroallylic groups is equal to $\sim 200\,min$ at 200°C (Fig. 4) [21, 24].

2.3. Comparison of the Kinetic Curves for the Thermal Dehydrochlorination of PVC with Effective Removal of HCl with the Theoretical Curves of the Thermal Degradation of the Low Molecular Weight Models of PVC Macromolecules

2.3.1. Comparison of the Kinetic Curves for PVC Degradation with the Theoretical Curves for Decomposition of Chlorohydrocarbons Containing Only VC Units

In the paper [25] it has been carried out the comparison of the experimental curves of the dependence of the dehydrochlorination rate on time which have been obtained by different authors [25, 28, 32, 38]

FIGURE 4   Calculated from Eq. (19) curves of the dependence of dehydrochlorination rate on time for the thermal degradation of chlorohydrocarbons, having VC units and the internal chloroallylic fragment, at different l_{av} and C^0_{all} at 200°C in inert solvent: (1) and (3) $l_{av} = 4$; (2) and (4) $l_{av} = 7$; (1) and (2) $C^0_{all} = 0.1$ mol%; (3) and (4) $C^0_{all} = 0.3$ mol% [21].
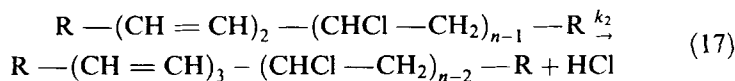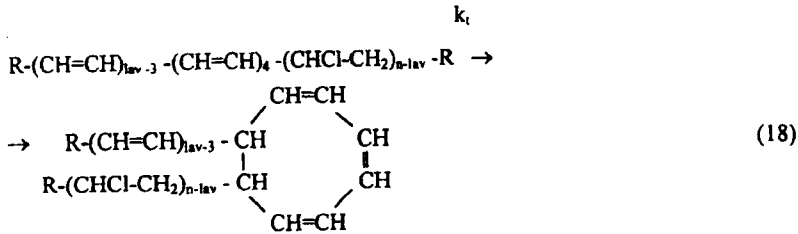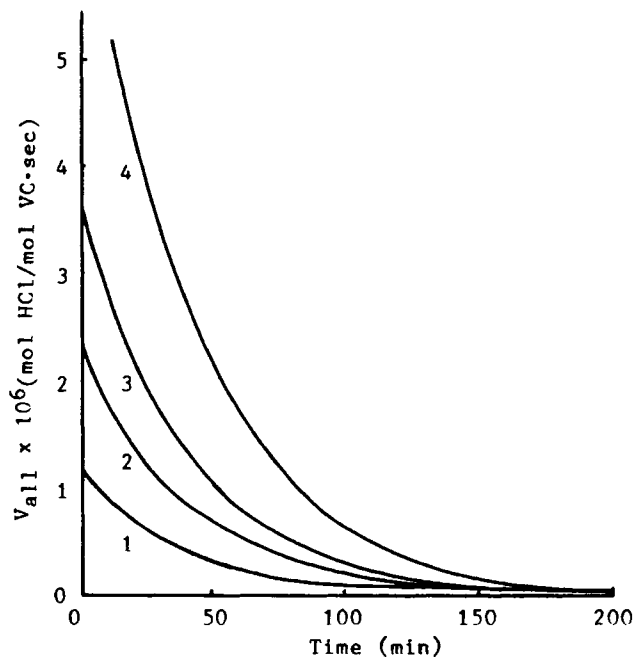
for the initial stage (upto 10% conversion) of the thermal degradation of more than 20 various samples of PVC with effective removal of HCl at 180–210°C with the theoretical curves for the thermal degradation of chlorohydrocarbons containing only VC units which are the low molecular weight model compounds for idealized PVC. The theoretical curves have been calculated from the Eq. (7) using the values of k_0 and k_1 which have been determined for the thermal degradation of chlorohydrocarbons in the liquid phase with removal of HCl [14, 15]. Data obtained in the paper [25] show clearly that the initial rates of degradation of the various samples of PVC (at $t \rightarrow 0$) are 3–30 (and more) times greater than the initial rates of dehydrochlorination of model chlorohydrocarbons having only VC units. This indicates that the thermal degradation of unstable fragments, present in the original polymer, make the main contribution into the initial rate of

degradation of PVC (at $t \to 0$). After a definite period of time ($\sim 100 -$ 150 min at 200°C) unstable groups, present in the original PVC, decompose and the stationary rate of dehydrochlorination of PVC samples is determined only by the rate aof degradation of the normal units of macromolecules [25]. It has been shown [25] that the stationary rates of dehydrochlorination of the various samples of PVC are not equal to each other and at most thrice differ from one another. But discrepancy between the stationary rates is considerably less than between the initial rates.

It has been considered two reasons which may lead to deviation of the values of the stationary rates of degradation of the various samples of PVC [25]. First, the concentration of HCl in the polymer particles of the various samples of PVC having complicated morphological structure, various sizes and density may differ from one another due to the different rates of diffusion of HCl from them. Secondly, the results show that the higher the initial rate of PVC dehydrochlorination, the greater the stationary one [25]. It has been proposed [25] that the more HCl eliminates at the beginning of PVC dehydrochlorination, the greater is the effect of HCl on the stationary rate. One can also assume that in the initial stage of the thermal degradation of PVC samples having increased values of the stationary rates, the new structures, which initiate the dehydrochlorination of the normal units of PVC macromolecules, form [48]. This will be discussed in detail below in Section 4.

Data, obtained in the paper [25], show that the stationary rates for the thermal dehydrochlorination of three various samples of PVC, namely of finely dispersed PVC powder (sample B), thin polymer film (sample I) and 1% 1,2,4-trichlorobenzene solution of PVC (sample H), which were decomposed with continuous and effective removal of HCl at 200°C at various conditions by different investigators [25, 28, 38], are practically the same and have the least value, $V_{\text{stat}}^{\text{min}} = 8 \times 10^{-7}$ -10×10^{-7} mol HCl/mol VC sec. It has been concluded [25] that $V_{\text{stat}}^{\text{min}}$ characterize the thermal degradation of PVC initiated by dehydrochlorination of only normal units of macromolecules without influence of HCl.

The value of $V_{\text{stat}}^{\text{min}}$ coincides with the calculated meaning of the stationary rate for degradation of model chlorohydrocarbons, containing only VC units, at $l_{\text{av}} \cong 0.9 - 1.3$ [25]. But one must bear in

mind that for calculations of the rate of degradation of model chlorohydrocarbons the value of $k_0 = 8.27 \times 10^{-7} \sec^{-1}$, which has been obtained for the thermal dehydrochlorination of 8-chlorohexadecane at 200°C in liquid phase [15], has been used (see Section 2.1). It has been showed that $l_{av} = 8$ for sample B [30] and $l_{av} = 10.4$ for sample H [28]. Using these experimental values of l_{av} and the value of V_{stat}^{min}, from the Eq. (9) one can obtain that at 200°C k_0 is equal to $1.3 \times 10^{-7} \sec^{-1}$ and $7.4 \times 10^{-8} \sec^{-1}$ for degradation of samples B and H respectively. Comparison of these values of k_0 with the value of k_0 for dehydrochlorination of 8-chlorohexadecane at 200°C shows that the latter is 6–11 times greater than the value of k_0 for degradation of VC units in PVC macromolecule.

Figures 5 and 6 the experimental curves of the dependence of the dehydrochlorination rate on time for degradation of samples B (Fig. 5) and H (Fig. 6) at 200°C and the calculated from the Eq. (7) curves of the dependence of the dehydrochlorination rate on time for degradation of model chlorohydrocarbons, containing only VC units, at the value of k_0, k_1 and l_{av}, which were obtained for samples B and H at the condition that $K_1 = k_{unstab}^{ef}$ [44]. The values of k_1 were taken from Table I.

It has been concluded [25] that comparison of the kinetic curves of the initial stage of the thermal degradation of PVC samples with the theoretical ones for decomposition of model compounds, containing only VC units, makes it possible to evaluate the summary contribution of degradation of unstable fragments present in the original PVC to the initial rate of dehydrochlorination of specific samples of PVC at $t \rightarrow 0$ quantitatively. It is seen from Figures 5 and 6.

2.3.2. Comparison of the Kinetic Curves for PVC Degradation with the Theoretical Curves for Decomposition of Mixture of Chlorohydrocarbon Having only VC Units with Compound Containing VC Units and Unstable Fragment

Using the Eqs. (6) and (20) and the expressions (7) and (19), one can obtain the following Eqs. (21) and (22) which describe the initial stage of degradation of mixture of chlorohydrocarbon, containing only VC units, with model compound having VC units and the internal
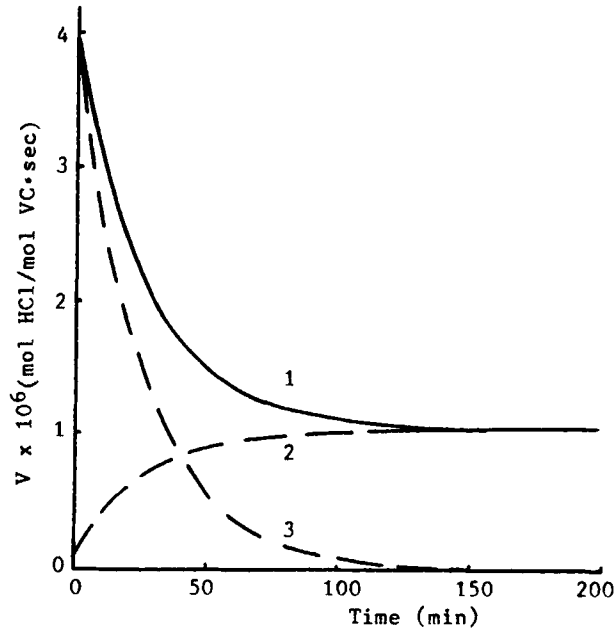
FIGURE 5 Dependence of dehydrochlorination rate on time at 200°C for thermal degradation of (1) PVC sample B in vacuo ($\sim 10^{-4}$ mm Hg) with continuous removal of HCl by freezing; (2) idealized PVC containing only VC units; (3) unstable fragments present in original PVC sample B [44]. Curve 2 is calculated from Eq. (7) at the meanings of parameters obtained for PVC sample B. Curve 3 is obtained by geometrical substraction of curve 2 from curve 1. B is sample from Ref. [25].

chloroallylic fragment:

$$[HCl]_1 = [HCl]_{norm} + [HCl]_{all} \qquad (21)$$

$$V_1 = V_{norm} + V_{all} \qquad (22)$$

The Eqs. (23) and (24) which were obtained from the Eqs. (6) and (15) and the Eqs. (7) and (14), describe the initial stage of the thermal degradation of mixture of chlorohydrocarbon, containing only VC units, with model compound having VC units and the branching fragment with the chlorine atom near the teritary carbon atom:

$$[HCl]_2 = [HCl]_{norm} + [HCl]_{ter} \qquad (23)$$

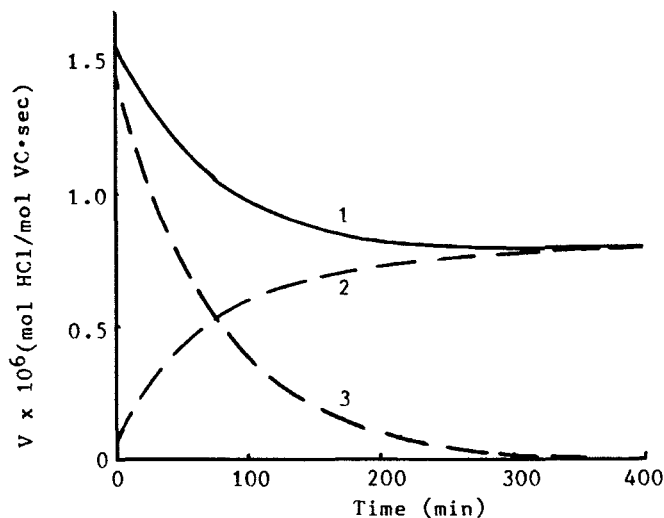$$V_2 = V_{norm} + V_{ter} \qquad (24)$$

FIGURE 6   Dependence of dehydrochlorination rate on time at 200°C for thermal degradation of (1) 1% solution of PVC in 1,2,4-trichlorobenzene (sample H) with continuous removal of HCl by stream of inert gas; (2) idealized PVC containing only VC units; (3) unstable fragments present in original PVC sample H [44]. Curve 2 is calculated from Eq. (7) at the meaning of parameters obtained for PVC sample H. Curve 3 is obtained by geometrical substraction of curve 2 from curve 1. H is sample from Ref. [28].

The summations of the Eqs. (6), (15) and (20) and the Eqs. (7), (14) and (19) gives the expressions (25) and (26) which describe the initial stage of decomposition of the triple mixture of model chlorohydrocarbons, containing only VC units, VC units and the internal chloroallylic group and VC units and the branching fragment with the chlorine atom near the teritary carbon atom, in any ratio:

$$[HCl]_3 = [HCl]_{norm} + [HCl]_{all} + [HCl]_{ter} \qquad (25)$$

$$V_3 = V_{norm} + V_{all} + V_{ter} \qquad (26)$$

Using the Eqs. (15) and (20) and the Eqs. (14) and (19), one can obtain the expressions (27) and (28) which describe the initial stage of degradation of mixture of model chlorohydrocarbon, containing VC units and the internal chloroallylic group, with model compound

having VC units and fragment with the chlorine atom near the tertiary carbon atom:

$$[HCl]_4 = [HCl]_{all} + [HCl]_{ter} \tag{27}$$

$$V_4 = V_{all} + V_{ter} \tag{28}$$

In the papers [21, 24] satisfactory coincidence of the theoretical curves of the thermal degradation of PVC calculated from the expressions (21) and (23) with experimental ones, has been obtained. In the papers [44, 49] it has been attained good coincidence of the theoretical curves of the thermal dehydrochlorination of various samples of PVC which were calculated from the Eqs. (21)–(28), with the experimental curves.

In the paper [49] integral and differential kinteic curves for the initial stage of the thermal degradation of nine samples of PVC in vacuo with continuous removal of HCl at 200°C have been obtained. It has been shown that these kinetic curves are well described by the expressions (21) and (22) respectively. The values of k^{ef}_{unstab} were calculated from the experimental curves of dehydrochlorination of PVC samples by the method proposed before [36, 37, 40, 41]. At 200°C they are equal to $2.8 \times 10^{-4} - 4.6 \times 10^{-4} \sec^{-1}$. The investigated samples of PVC were calculated to contain $0.1-0.3$ mol% of unstable fragments. There is the correlation between the total concentration of unstable groups in PVC samples and the initial rate of degradation of the polymers [49]. The obtained values of k^{ef}_{unstab} for PVC samples are close to the rate constants for the thermal degradation of the low moleuclar weight model chlorohydrocarbons having the branching groups with the chlorine atom near the tertiary carbon atom or the internal chloroallylic fragments in the liquid phase [14, 15, 47]. It has been concluded that these groups may be the main unstable fragments of PVC macromolecules [49].

It is of interest of consider data which has been obtained for PVC samples having known quantity of unstable fragments [44]. In the paper [28] the series of PVC samples, containing various quantity of the internal chloroallylic groups, has been prepared by controled chemical dehydrochlorination of the same sample of PVC (sample H) at low

temperature. The thermal degradation of 1% 1,2,4-trichlorobenzene solution of these samples has been studied with effective removal of HCl. By geometrical substraction of the kinetic curve of dehydrochlorination of sample H having $C_{all}^0 = 6 \times 10^{-5}$ mol/mol VC from the kinetic curve of degradation of sample K having $C_{all}^0 = 1.07 \times 10^{-3}$ mol/mol VC the kinetic curve of dehydrochlorination of PVC initiated by degradation of the internal chloroallylic fragments has been obtained at $C_{all}^0 = 1.01 \times 10^{-3}$ mol/mol VC (Fig. 7 curve 1) [44]. Figure 7 (curve 2) shows the theoretical curve of PVC dehydrochlorination initiated by degradation of the internal chloroallylic groups which was calculated from the Eq. (20) at the same value of C_{all}^0 and at $k_1 = 2.55 \times 10^{-4}$ sec^{-1} and $l_{av} = 11.045$. In the paper [28] practically the same values of l_{av} have been determined for sample H ($l_{av} = 10.4$) and sample K ($l_{av} = 11.6$). From curve 1 (Fig. 7) one can obtain the value of $\tau_{1/2}$. Using this value of $\tau_{1/2}$ it is possible to calculate $k_{unstab}^{ef} = 2.6 \times 10^{-4}$ sec^{-1} at 200°C. In this case k_{unstab}^{ef} is k_1, i.e., the constant of the rate of degradation of the internal chloroallylic fragments of PVC macromolecules. Thus, data, obtained in the papers [28, 44] make it possible to evaluate k_1 in the thermal degradation of PVC.

Figure 8 represents the integral [Fig. 8(a)] and differential [Fig. 8(b)] kinetic curves of dehydrochlorination of sample H at 200°C (curves 1).
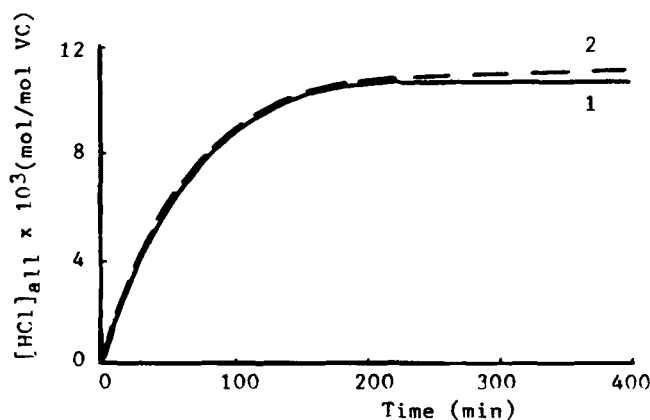
FIGURE 7   Kinetic curve of dehydrochlorination of internal chloroallylic fragments of PVC at 200°C (1). Curve 2 is calculated from Eq. (20) [44].

FIGURE 8 Integral (a) and differential (b) kinetic curve of dehydrochlorination of 1% solution of PVC in 1,2,4-trichlorobenzene (sample H) with con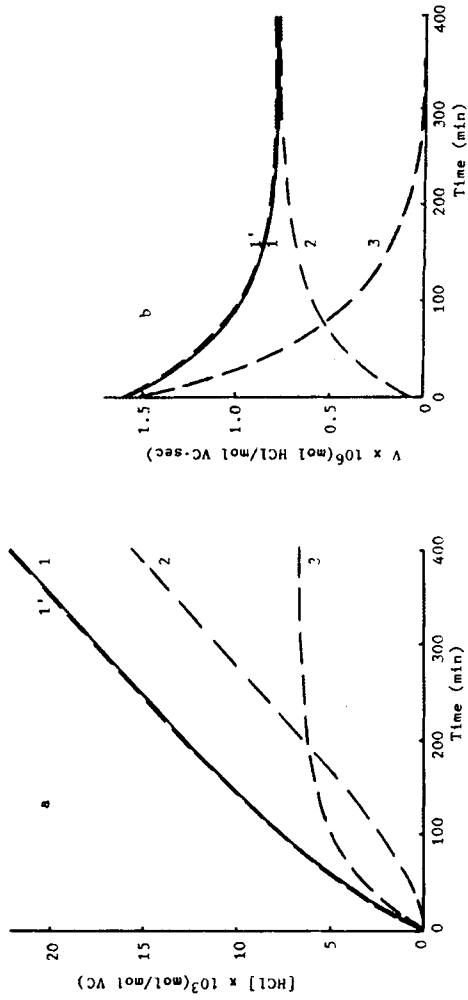tinuous removal of HCl by stream of inert gas at 200°C (1). Curves 1′, 2 and 3 are calculated from Eqs. (21) (a) and (22) (b); Eqs. (6) (a) and (7) (b); Eqs. (20) (a) and (19) (b) respectively [44]. H is sample from Ref. [28].

The theoretical curves 1′, 2 and 3 were obtained under the assumption that sample H has only the internal chloroallylic groups as unstable fragments [44]. The curves 1′, 2 and 3 were calculated at the same values of parameters from the Eqs. (21) [Fig. 8(a)] and (22) [Fig. 8(b)], the expressions (6) [Fig. 8(a)] and (7) [Fig. 8(b)] and (20) [Fig. 8(a)] and (19) [Fig. 8(b)], respectively. Curve 1′ corresponds to the geometircal sum of Curves 2 and 3. The theoretical Curve 1′ coincides with the experimental Curve 1 at the following values of parameters: $k_0 = 7 \times 10^{-8} \sec^{-1}$, $C^0_{all} = 6 \times 10^{-4}$ mol/mol VC, $l_{av} = 11.045$ and $k_1 = 2.3 \times 10^{-4} \sec^{-1}$. It is necessary to note that the value of k_1 corresponds to the value of k^{ef}_{unstab} which was determined for sample H from the value of $\tau_{1/2}$ (Tab. I). The meanings of k_0 and l_{av} coincide practically with the meanings of these parameters obtained in the paper [28]. But the value of C^0_{all} which was chosen for coincidence of the theoretical curve 1′ with the experimental curve 1, is 10 times greater than that determined for sample H in the paper [28]. One may assume that sample H has not only the internal chloroallylic fragments but other unstable groups as well.

Figure 9 shows the theoretical curves of PVC dehydrochlorination (curves 1′, 2 and 3) which were obtained under the assumption that in sample H there are the internal chloroallylic fragments and the branching groups with the chlorine atom near the tertiary carbon atom, the concentration of the internal chloroallylic fragments being equal to that determined in the paper [28]. The theoretical curves 1′, 2 and 3 were calculated at the same meanings of parameters from the Eqs. (25) [Fig. 9(a)] and (26) [Fig. 9(b)], the Eqs. (6) [Fig. 9(a)] and (7) [Fig. 9(a)] and the Eqs. (27) [Fig. 9(b)] and (28) [Fig. 9(b)], respectively. The coincidence of the experimental curve 1 with the theoretical curve 1′ is observed at the following meanings of parameters: $k_0 = 7 \times 10^{-8}$ sec^{-1}, $C^0_{all} = 6 \times 10^{-5}$ mol/mol VC, $k_1 = 2.3 \times 10^{-4} \sec^{-1}$, $C^0_{ter} = 5.45 \times 10^{-4}$ mol/mol VC, $k_{ter} = 2.31 \times 10^{-4} \sec^{-1}$ and $l_{av} = 11.045$. From Figure 9(b) one can see that in this case the differential theoretical curves 1′ and 3 have maximum at small times of degradation. Thus, it has been shown that the initial stage (upto $\sim 10\%$ conversion) of the thermal dehydrochlorination of PVC may be described by the Eqs. (21)–(26) which have been deduced under the supposition that the thermal degradation of PVC initiates by decomposition of normal units and unstable fragments such as the

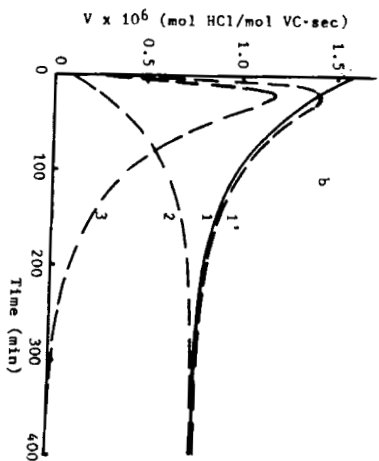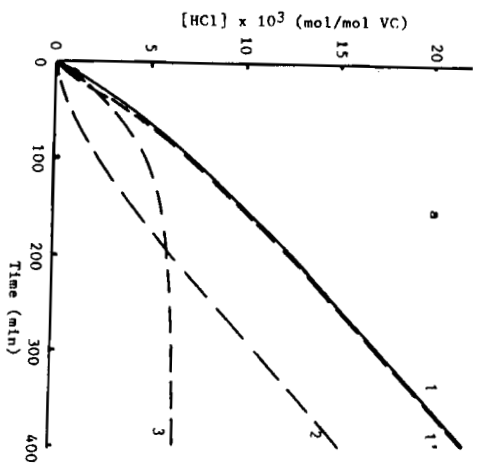FIGURE 9   Integral (a) an differential (b) kinteic curve of dehydrochlorination of 1% solution of PVC in 1,2,4-trichlorobenzene (sample H) with continuous removal of HCl by stream of inert gas at 200°C (1). Curves 1', 2 and 3 are calculated from Eqs. (25) (a) and (26) (b); Eqs. (6a) and (7) (b); Eqs. (27) (a) and (28) (b) respectively [44]. H is sample from Ref. [28].

internal chloroallylic groups and the branching fragments with the chlorine atom near the tertiary carbon atom.

3. MATHEMATICAL MODELS OF THE INITIAL STAGE OF THE THERMAL DEGRADATION OF PVC OBTAINED BY MEANS OF NUMERICAL SOLUTION OF THE SYSTEMS OF THE DIFFERENTIAL EQUATIONS

3.1. The Thermal Degradation of PVC Initiated by Decomposition of Normal Units and the Internal Chloroallylic Fragments

In the paper [26] the mathematically models for the initial stage of thermal degradation of PVC have been examined using the program given in the book [50] for solution of the systems of the differential equations according to Euler's method with a computer under the same assumptions as in Section 2.

The mathematical models for the thermal degradation of PVC initiated by decomposition of normal units and the internal chloroallylic fragments, have been considered [26]. The theoretical curves for PVC dehydrochlorination at 200, 240 and 250°C have been calculated. It has been shown that these curves coincide with the experimental ones up to $\sim 30-40\%$ conversion. It has been demonstrated that there is coincidence of these theoretical curves with curves calculated from the Eq. (21) at the same values of k_0, k_1 and C_{all}^0. Results obtained in the paper [26] give the evidence of the validity of the equations which have been previously [16–24] deduced for the initial stage (upto $\sim 10\%$ conversion) of PVC degradation initiated by decomposition of normal units and unstable fragments such as the internal chloroallylic groups, the branching fragments with the chlorine atom near the tertiary carbon atom or sum of these fragments in all proportions [the Eqs. (21)–(26)]. The mathematical models proposed in the paper [26] make it possible to describe the initial stage of the thermal degradation of PVC upto $\sim 30-40\%$ conversion.

3.2. Influence of Tacticity of Macromolecules on the Thermal Degradation of PVC

Only a few papers have dealt with the influence of tacticity of macro-molecules on the thermal degradation of PVC [5, 26, 49, 51 – 53]. It has been shown [52] that in the thermal degradation of PVC above the glass transition temperature the polyene length distribution is characterized by a high amount of very short polyenes. Below the glass transition temperature the formation of much long polyenes is observed due to degradation of highly syndiotactic sequences in macro-molecules [52]. It has been established [53] that the bulk and suspension polymers prepared at very low conversions (0.1 – 2%) differ from those obtained at high conversions (70%). The former polymers have more syndiotactic sequences and are less thermostable at 190°C, more long polyenes form in the thermal degradation of these polymers.

On the other hand, it has been proposed [51] that the thermal degradation of PVC is the stereoselective reaction, and isotactic triads (mm) decompose with a greater rate than syndio (rr) or heterotactic (rm) triads. The reactivity of isotactic triads is higher as the length of the isotactic sequence ending with -mmr-, increases. The conclusion has been drawn [51] that the very labile structure in PVC are some chlorine atoms located mainly at the normal GTTG* isotactic triad conformation in the -mmr- structures which are at the end of some definite isotactic sequences. The content of this conformation has been estimated to lie between 0.2% and 0.8% depending on the overall isotactic content of the sample of PVC [51].

In the paper [49] the tacticity of nine various samples of suspension PVC has been measured by ^{13}C NMR spectroscopy. Configuration of PVC macromolecules is described by Bernoullian statistic of chain growth and is determined by probability of meso- addition, P_m [54]. In the paper [49] using ^{13}C NMR data, the values of P_m were calculated and the contents of tactic sequences were evaluated in PVC samples. The dehydrochlorination of PVC samples under vacuum with continuous removal of HCl has been studied at 200°C. The total concentration of unstable groups in PVC samples has been deter-mined. It has been established that only the contents of isotactic

nonads may be compared with the values of concentrations of the unstable fragments in the samples. There is no correlation between the initial rate of PVC degradation and the content of isotactic triads or nonads in the samples [49]. It is interesting to note that the correlation between V_{stat} and the content of isotactic triads is absent too [49]. It has been shown [49] that the values of rate constants for the thermal degradation of two stereoisomers, d, l-2,4-dichloropentane and *meso*-2,4-dichloropentane, in the liquid phase at 200°C are practically the same and do not depend on stereoisomery of compounds. The results obtained in the paper [49] give evidence that the tacticity of macromolecules has no significant influence on the intital stage of the thermal degradation of PVC.

The mathematical model for the initial stage of the thermal degradation of PVC has been proposed at the assumption that tacticity of macromolecules has the greatest influence on the thermal stability of the polymer [26]. It has been supposed that the PVC degradation is initiated by decomposition of normal units and the unstable conformer of the definite isotactic isomer (isotactic heptad, octad or nonad). It has been shown that there is no coincidence between the experimental kinetic curve for PVC dehydrochlorination and the theoretical ones. The theoretical curves of PVC degradation are S-shaped ones. The greater the concentration of the isotactic isomer, the greater the discrepancy between the theoretical curves of PVC dehydrochlorination and the experimental one. The conclusion has been made that at elevated temperatures the thermal degradation of PVC is not the stereoselective reaction [26].

4. MECHANISM OF THE NONAUTOCATALYTIC THERMAL DEGRADATION OF PVC

Two theories have been offered for the nonautocatalytic thermal degradation of PVC with effective removal of HCl: the molecular and the radical theories [3–10, 12–14, 27, 55, 56].

In accordance with the radical theory, the chlorine atoms and macroradicals are the main active particles in the thermal degradation of PVC. It is well known that metals are the effective acceptors of the chlorine atoms. It has been established [36, 37] that some metals

(mercury, silver) which do not react with HCl, do not influence on the rate of the nonautocatalytic thermal degradation of PVC with effective removal of HCl.
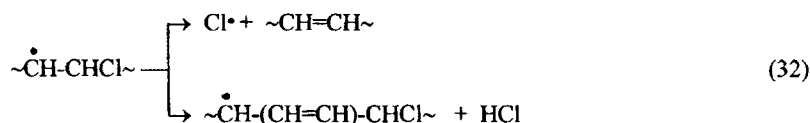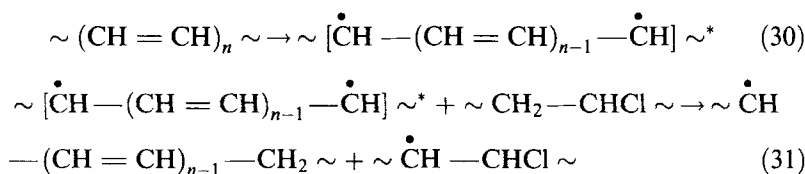
Recently [57] it has been shown that fullerence C_{60} retards the thermal depolymerization of poly (methyl methacrylate) (PMMA) and does not influence on the nonautocatalytic thermal dehydrochlorination of PVC with effective removal of HCl. It is well known [58] that C_{60} reacts easily with low molecular weight free radicals with formation of relatively stable particles. The thermal depolymerization of PMMA is the chain radical reaction [59]. It is assumed [57] that the inhibiting influence of C_{60} on PMMA in its thermal degradation is connected with interaction of fullerence with macroradicals. These data indicate that the nonautocatalytic PVC degradation with effective removal of HCl proceeds mostly by the molecular mechanism. On the basis of the numerous experimental data concerning the thermal degradation of the low molecular weight model chlorohydrocarbons, the molecular mechanism has been proposed for this process [14, 60, 61]. This supports the molecular mechanism of the nonautocatalytic thermal degradation of PVC too.

The following data confirm that in the nonautocatalytic PVC degradation radical processes take place. It is well known that in the thermal degradation of PVC at $180-210°C$ benzene evolves in small quantities ($100-1000$ times less than the quantity of HCl) [4–10, 29, 34, 37, 56]. Inhibitors of free radical reactions, such as nitrogen oxide and α-naphthol decrease the rate of its formation in the nonautocatalytic degradation of PVC with effective removal of HCl [34, 56]. Peroxides and hydroperoxides which are present in PVC in small quantities, increase the initial rate of PVC dehydrochlorination [3, 5, 55, 62–64]. In the papers [10, 11, 27, 29, 35] it has been suggested that the nonautocatalytic thermal degradation of PVC mostly proceeds by a molecular mechanism complicated by radical reactions. In the papers [35, 48, 65] the more probable reactions of initiation of the nonautocatalytic thermal degradation of PVC by the radical mechanism have been proposed. The role of thermally excited states of polyenes and polyenyl carbocations in the thermal degradation of PVC has been discussed. Data concerning dependences of energies of electron transitions from the basic level (S_0) to first excited singlet level (S_1) and from S_0 to the first triplet level (T_1) and of energy barriers for
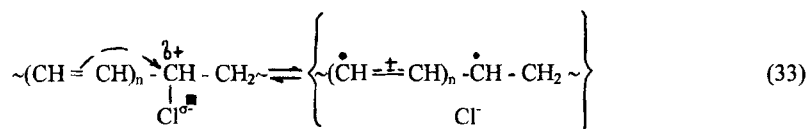
rotation about central double bond in polyenes and polyenyl carbocations on n have been considered [48]. It is known that *cis*–trans rearrangement of polyenes is one of the reactions which characterize their reactivity. The thermal monomolecular reaction of *cis*-trans rearrangement of polyenes proceeds *via* excited triplet state [66–68]:
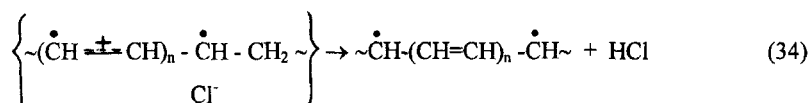
 (29)
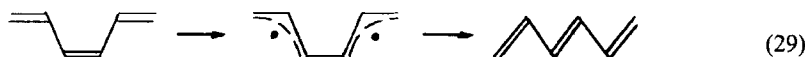
Using experimental data [66–68] concerning the thermal *cis*–trans rearrangement of all-trans-β-carotene, the low molecular weight model of polyene fragments of PVC, it has been shown [48] that at $180–200°C$ reactivity of polyenes having ≥ 8 conjugated double bond is great. The assumption has been made that in PVC degradation polyenes in excited triplet state (biradical state) may take part in different radical reactions, in particular, in the reaction of initiation of polymer dehydrochlorination [35, 48, 65]:

$$\sim (CH = CH)_n \sim \to \sim [\overset{\bullet}{C}H - (CH = CH)_{n-1} - \overset{\bullet}{C}H] \sim^* \quad (30)$$

$$\sim [\overset{\bullet}{C}H - (CH = CH)_{n-1} - \overset{\bullet}{C}H] \sim^* + \sim CH_2 - CHCl \sim \to \sim \overset{\bullet}{C}H$$

$$- (CH = CH)_{n-1} - CH_2 \sim + \sim \overset{\bullet}{C}H - CHCl \sim \quad (31)$$

$$\sim\overset{\bullet}{C}H\text{-}CHCl\sim \longrightarrow \begin{cases} Cl^{\bullet} + \sim CH=CH\sim \\ \\ \sim\overset{\bullet}{C}H\text{-}(CH=CH)\text{-}CHCl\sim + HCl \end{cases} \quad (32)$$

Reactivity of polyenyl carbocations is greater than that of polyenes because the energy of excitation of them into triplet state is less. It has been shown [48] that the activation energies of the thermal decomposition of the low molecular weight model chlorohydrocarbons having one or two conjugated double bonds, in the liquid phase with removal of HCl agree closely with the energies of $S_0 \to T_1$ electron transitions in polyenyl carbocations. In the excited triplet state polyenyl carbocation is carbocation-biradical. The following reaction of the thermal dehydrochlorination of polyenyl fragment has been proposed under the assumption that the main elementary act of the reaction is intramolecular transference of electron [48, 65]:

$$\sim(CH \overset{\frown}{=} CH)_n \overset{\delta+}{\overset{\bullet}{C}H} - CH_2 \sim \rightleftharpoons \left\{ \sim(\overset{\bullet}{C}H \overset{\pm}{=} CH)_n \cdot \overset{\bullet}{C}H - CH_2 \sim \right\} \tag{33}$$

Then subsequent transformation of ion-biradical pair into biradical may occur [48, 65]:

$$\left\{ \sim(\overset{\bullet}{C}H \overset{\pm}{=} CH)_n - \overset{\bullet}{C}H - CH_2 \sim \atop Cl^- \right\} \rightarrow \sim\overset{\bullet}{C}H\text{-}(CH=CH)_n \text{-}\overset{\bullet}{C}H\sim + HCl \tag{34}$$

Forming biradical may initiate the thermal degradation of PVC by the radical mechanism [the Eqs. (31) and (32)] [48, 65].

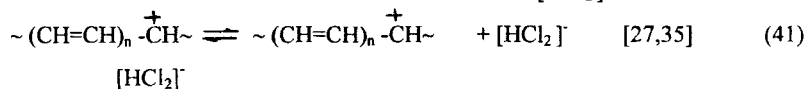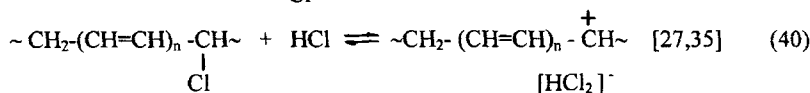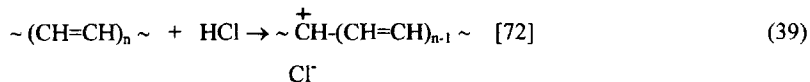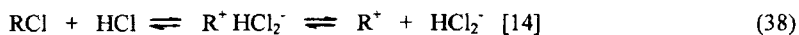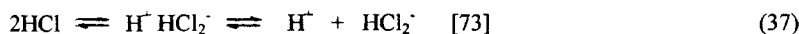The expressions (31)–(34) represent the most probable reactions of the initiation of the degenerated branching of chain in the thermal degradation of PVC with removal of HCl. It follows that this porcess must be an autocatalytic one. In fact in the thermal dehydrochlorination of PVC with effective removal of HCl autocatalysis is not observed (see Section 1). As discussed in the paper [48], the reactions of cyclization decrease the concentration of long polyenes and increase the concentration of short ones. As mentioned above, in the thermal degradation of PVC with effective removal of HCl $l_{av} = 8-15$ [28–30, 45], the average number of conjugated double bonds in formed polyenes which has been determined by the use of absorption spectra of degraded PVC, is equal to 3–10 [5, 28, 69]. The energy of excitation of short polyenes to the triplet state is more than long ones [48]. It has been concluded [48, 65] that in the thermal degradation of PVC with effective removal of HCl probability of the reactions (31)–(34) is little therefore the degenerated branching of chain proceeds with small rate. One cannot also exclude the possibility of removal of active particles – atomic chlorine from zone of the reaction in the thermal degradation of PVC with effective removal of HCl [35].

5. MECHANISM OF AUTOCATALYTIC THERMAL DEGRADATION OF PVC

As mentioned above (see Section 1) the thermal degradation of PVC is complicated by the catalytic effect of evolving HCl. In the presence of

HCl the thermal dehydrochlorination of the polymer has an auto-catalytic character [10, 25, 27, 29, 32, 33, 35 – 37]. The initial rate of degradation has a minimum value and then the rate of PVC dehydrochlorination increases up to maximum value. The maximum rate is some 10 times greater that the initial one.

The thermal degradation of PVC in the presence of HCl is generally believed to proceed by an ionic or molecular mechanism [5, 9 – 14, 27, 33, 35, 70 – 73]. Some reaction schemes have been offered [the Eqs. (35) – (41)]:

$$\sim CH_2 - \underset{\substack{\overset{|}{C}l \\ \overset{|}{H} \diagup Cl}}{CH} \underset{\substack{\overset{\diagdown}{H}}}{CH} - CHCl\sim \;\rightarrow\; \sim CH_2\text{-}CH\text{=}CH\text{-}CHCl\sim \;\; + HCl \quad [70] \tag{35}$$

$$\sim(CH\text{=}CH)_n - \underset{\substack{\overset{|}{Cl} \\ \overset{|}{H} - \overset{|}{Cl}}}{CH} - \underset{\substack{\overset{|}{H}}}{CH}\sim \;\rightarrow\; \sim(CH\text{=}CH)_{n+1} \sim + \; 2HCl \quad [33,35] \tag{36}$$

$$2HCl \;\rightleftharpoons\; H^+HCl_2^- \;\rightleftharpoons\; H^+ + HCl_2^- \quad [73] \tag{37}$$

$$RCl + HCl \;\rightleftharpoons\; R^+HCl_2^- \;\rightleftharpoons\; R^+ + HCl_2^- \quad [14] \tag{38}$$

$$\sim(CH\text{=}CH)_n \sim \; + \; HCl \rightarrow \sim \overset{+}{C}H\text{-}(CH\text{=}CH)_{n-1} \sim \quad [72] \tag{39}$$
$$Cl^-$$

$$\sim CH_2\text{-}(CH\text{=}CH)_n\text{-}\underset{\substack{\overset{|}{Cl}}}{CH}\sim \; + \; HCl \;\rightleftharpoons\; \sim CH_2\text{-}(CH\text{=}CH)_n\text{-}\overset{+}{C}H\sim \quad [27,35] \tag{40}$$
$$[HCl_2]^-$$

$$\sim(CH\text{=}CH)_n\text{-}\overset{+}{C}H\sim \;\rightleftharpoons\; \sim(CH\text{=}CH)_n\text{-}\overset{+}{C}H\sim \; + [HCl_2]^- \quad [27,35] \tag{41}$$
$$[HCl_2]^-$$
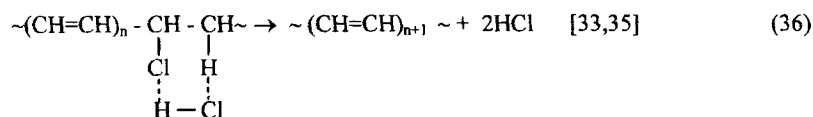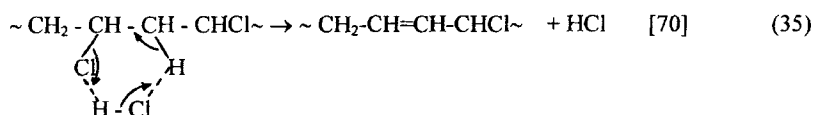
It is necessary to note that PVC is chlorohydrocarbon having small dielectric penetration [4]. In these media the probability of dissociation of ionic pairs into free ions is small. Therefore in the initial stage of the autocatalytic thermal degradation of PVC (upto ~10% conversion) there is small possibility of the presence of free ions in accordance with reactions (37) – (39) and (41). It is more probable to suppose that in the autocatalytic thermal degradation of PVC contact ionic pairs are active particles [the Eq. (40)]. But there are numerous experimental

data which testify that in the thermal degradation of PVC in the presence of HCl radical reactions take place. These data are considered below.

5.1. Mathematical Models of the Initial Stage of the Autocatalytic Thermal Degradation of PVC

Several mathematical models for the initial stage of the thermal degradation of PVC in the presence of HCl have been proposed taking into consideration the different mechanisms for the autocatalytic degradation of the polymer [74, 75]. The theoretical curves are compared with the kinetic curves of the thermal degradation of PVC. It has been shown [74, 75] that the kinetic curves of PVC autocatalytic dehydrochlorination at a constant pressure of HCl during an experiment are described by the expression (42) at the value of branching factor $\varphi = 1 - 1.5 \times 10^{-4}$:

$$[HCl]_S = [HCl]_{norm} + A(e^{\varphi t} - 1) \qquad (42)$$

where $[HCl]_S$ is summary quantity of HCl evolving during non-autocatalytic and autocatalytic dehydrochlorination of PVC; $[HCl]_{norm}$ is calculated from the Eq. (6).

The expression $A(e^{\varphi t} - 1)$ is typical for the kinetics of branched chanin reactions [76] where A and φ are constant values.
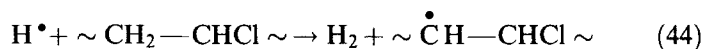
5.2. Retarding Effect of Compounds which do not React with HCl on the Autocatalytic Thermal Degradation of PVC

It has been established that maleic anhydride, active dienophil, which does not react with HCl and ineracts easily with polyenes by the Diels-Alder reaction, suppresses the autocatalytic dehydrochlorination of PVC [33, 35, 77–80]. It has been concluded that the accelerating effect of HCl is marked when there are sections of conjugated double bonds in PVC macromolecules [33, 35, 77–80]. This conclusion is supported by the following experiments. It has been shown that the longer degradation in vacuo proceeded, the more polyene areas formed, and the higher the initial dehydrochlorination rate with the HCl addition

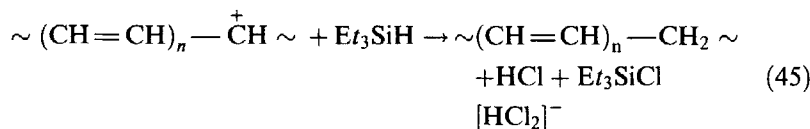became [35,78]. The thermal degradation of 8-chlorohexadecane and 8-chloro-6-tridecylene which are the low molecular weight model compounds for normal units of PVC and chloroallylic fragments respectively, in the liquid phase has been studied [14, 15]. It has been shown that HCl has to influence on the thermal degradation of 8-chlorohexane and accelerates the thermal dehydrochlorination of 8-chloro-6-tridecylene. Consequently, one can propose that HCl does not affect the thermal degradation of normal units of PVC and increases the rate of dehydrochlorination of fragments having double (conjugated double) bonds,

$$\sim (CH{=}CH)_n{-}CHCl \sim .$$
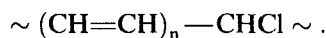
The autocatalytic dehydrochlorination of PVC is suppressed by triethyl silane which does not react with HCl under the conditions at which the thermal degradation of PVC is carried out [81]. In this process the formation of $H_2(\sim 0.1$ part of the quantity of evolved HCl) takes place. The elimination of H_2 is proof of the presence of free radicals [the Eqs. (43) and (44)] [81]:

$$Cl^\bullet + Et_3SiH \rightarrow Et_3SiCl + H^\bullet \qquad (43)$$

$$H^\bullet + \sim CH_2{-}CHCl \sim \rightarrow H_2 + \sim \overset{\bullet}{C}H{-}CHCl \sim \qquad (44)$$
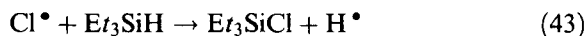
When the thermal degradation of PVC in the presence of Et_3SiH is carried out with addition of HCl, the rate of PVC dehydrochlorination does not increase, but in degraded polymer the quantity of long polyenes decreases. The latter is supported by absorption spectra of degraded PVC [81]. It has been proposed that HCl is the catalyst of the reaction of Et_3SiH with polyene fragments [the Eqs. (40) and (45)] [29]:

$$\sim (CH{=}CH)_n{-}\overset{+}{C}H \sim + Et_3SiH \rightarrow \sim (CH{=}CH)_n{-}CH_2 \sim$$
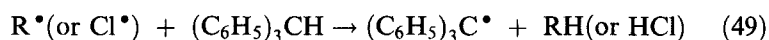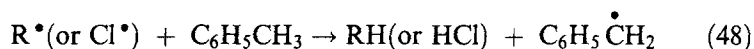$$+HCl + Et_3SiCl \qquad (45)$$
$$[HCl_2]^-$$

During PVC degradation in evacuated ampoules in the presence of mercury or silver, autocatalysis does not take place [36, 37, 82]. This metals do not interact with HCl, but react easily with atomic chlorine. Mercury may form two chlorides: $HgCl_2$ and Hg_2Cl_2. In the thermal

degradation of PVC in the presence of mercury Hg_2Cl_2 was determined only [36, 37, 82]. It has been assumed that in this process the following reactions proceed [36, 37, 82]:

$$Cl^\bullet + Hg \rightarrow {}^\bullet HgCl \tag{46}$$

$$2\overset{\bullet}{H}gCl \rightarrow Hg_2Cl_2 \tag{47}$$

It has been shown [35, 78] that triphenylmethane and toluene which are the inhibitors of the free radical reactions, decrease the rate of the autocatalytic dehydrochlorination of PVC. One can suggest that the following reactions may occur:

$$R^\bullet(\text{or } Cl^\bullet) + C_6H_5CH_3 \rightarrow RH(\text{or } HCl) + C_6H_5\overset{\bullet}{C}H_2 \tag{48}$$

$$R^\bullet(\text{or } Cl^\bullet) + (C_6H_5)_3CH \rightarrow (C_6H_5)_3C^\bullet + RH(\text{or } HCl) \tag{49}$$

The reaction (48) is supported by the following data. It has been established [83] that in the thermal degradation of PVC in the presence of toluene labeled with tritium ($C_6H_5CH_2T$), tritium introduces into the polymer.

As mentioned above (see Section 4), fullerene C_{60} retards the process of the radical thermal depolymerization of PMMA [57]. It has been shown [57] that fullerene C_{60} decreases the rate of the autocatalytic dehydrochlorination of PVC too. Experiments show that C_{60} does not react with HCl under the conditions of carrying out the autocatalytic degradation of PVC. It has been assumed that retarding effect of C_{60} in the autocatalytic dehydrochlorination of PVC is connected with its interaction with free radicals [57]:

$$mR^\bullet(\text{or } mCl^\bullet) + C_{60} \rightarrow (mR)C_{60}[\text{or } (m\,Cl)C_{60}] \tag{50}$$

It has been demonstrated that PVC mixed with other polymers initiates the radical reactions of the thermal degradation of these polymers [84–88].

Intriguing data were obtained recently in the paper [89]. By ESR spectroscopy it has been shown that in thermally degraded PVC the
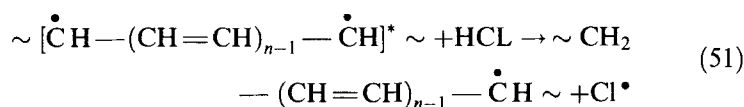
concentration of stable paramagnetic centers increases considerably if the polymer is decomposed in the presence of HCl.

5.3. Autocatalytic Thermal Degradation of PVC as the Branched Chain Reaction with the Degenerated Branching of Chain
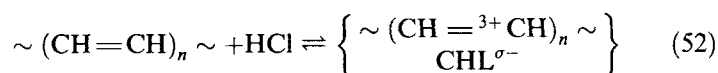
In the papers [48, 65, 74, 75, 89] the new theory is developed for the autocatalytic thermal degradation of PVC. It has been supposed that this process is the branched chain reaction with the degenerated branching of chain.

As mentioned above (see Section 4), it has been shown [35, 48, 65] that the reactions with participation of polyenes and polyenyl carbocations excited into triplet state [the Eqs. (31)–(34)] lead to the degenerated branching of chain in the thermal degradation of PVC, but probability of them is little.

In the thermal degradation of PVC in the presence of HCl the reaction (51) which initiates the degenerated branching of chain, may take place [35]:

$$\sim [\overset{\bullet}{C} H\text{---}(CH\text{=}CH)_{n-1}\text{---}\overset{\bullet}{C} H]^* \sim +HCL \rightarrow \sim CH_2$$
$$\text{---}(CH\text{=}CH)_{n-1}\text{---}\overset{\bullet}{C} H \sim +Cl^{\bullet} \tag{51}$$

It has ben demonstrated [27, 35, 74, 75] that two types of complexes of HCl (electrophilic agent) with polyenes are possible [the equations (40) and (52)].

$$\sim (CH\text{=}CH)_n \sim +HCl \rightleftharpoons \left\{ \begin{array}{c} \sim (CH\text{=}^{3+}CH)_n \sim \\ CHL^{\sigma-} \end{array} \right\} \tag{52}$$

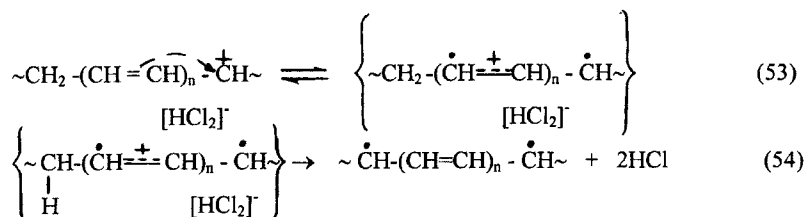These complexes are the contact ionic pairs. The Eq. (52) demonstrates the formation of the charge transfer complex. The complex by the Eq. (40) is molecular one.

The reaction scheme of the autocatalytic thermal degradation of PVC initiated by the Eq. (52) has been considered in the paper [89]. From this scheme it follows that H_2 must form. But experiments have shown that during the thermal degradation of PVC in the presence of

HCl H_2 does not practically evolve [89]. The conclusion has been made that it is unlikely that initiation of the autocatalytic degradation of PVC proceeds by the reaction (52) [89].

Consider the Eq. (40) now. In the paper [90] it has been shown that as a result of interaction of chlorine anion, Cl^-, with HCl with formation of $[HCl_2]^-$ the energy equal to ~ 14 Kcal/mol releases. It has been demostrated [48] that activation energies for the thermal degradation of low molecular weight models of polyenyl fragments of PVC macromolecules, which have one or two conjugated double bonds, in the liquid phase in the presence of HCl are in the field of triplet state of polyenyl carbocations. It has been concluded [48, 65] that probability of the reactions (53) and (54) is greater than the reactions (33) and (34).

$$\sim CH_2 - (CH = \overline{CH})_n \overset{+}{\cdot} CH \sim \; \rightleftharpoons \; \left\{ \sim CH_2 - (\overset{\bullet}{CH} \overset{+}{=\!\!=} CH)_n - \overset{\bullet}{CH} \sim \right\} \qquad (53)$$
$$\underset{[HCl_2]^-}{} \qquad\qquad\qquad\qquad \underset{[HCl_2]^-}{}$$

$$\left\{ \sim \underset{\overset{|}{H}}{CH} - (\overset{\bullet}{CH} \overset{+}{=\!\!=} CH)_n - \overset{\bullet}{CH} \sim \right\} \rightarrow \; \sim \overset{\bullet}{CH} - (CH = CH)_n - \overset{\bullet}{CH} \sim \; + \; 2HCl \qquad (54)$$
$$\qquad\qquad\quad [HCl_2]^-$$

It has been supposed [48, 65] that in the autocatalytic thermal degradation of PVC the reactions (51), (53) and (54) make the principal contribution to the degenerated branching of chain. HCl shows as the catalyst of the reactions of degenerated branching of chain [the Eqs. (51), (53) and (54)] which proceed with small rate in the non-autocatalytic thermal degradation of PVC too [the Eqs. (31) – (34)].

CONCLUSION

The review demonstrates that in the recent years there is a certain progress in some aspects of the thermal degradation of PVC. In the papers of recent years it has been shown that the mathematical models of the initial stage of the thermal decomposition of the low molecular weight model chlorohydrocarbons having only VC units and model

compounds, containing VC units and unstable fragments, have made it possible

- to investigate kinetic perculiarities of the initial stage (upto $\sim 10\%$ conversion) of the nonautocatalytic thermal dehydrochlorination of PVC quantitatively;
- to show that low molecular weight chlorohydrocarbons which may serve as models for PVC macromolecules, must contain 15 units of VC at the mimimum;
- to evaluate the summary contribution of unstable fragments present in the original polymer to the initial rate of PVC degradation at $t \to 0$ quantitatively. It has been demonstrated that the internal chloroallylic fragments and branching groups with the chlorine atom near the tertiary carbon atom may be the main unstable fragments of PVC macromolecules. But one cannot exclude the influence of other unstable groups on the initial rate of the thermal degradation of PVC, such as oxygen-containing fragments. The additional investigations are necessary in this direction

- to show that above $\sim 2-3\%$ conversion the thermal dehydro-chlorination of PVC is initiated by the statictic degradation of the normal units of polymer;
- to show that at elevated temperatures ($180-200°C$) the thermal degradation of PVC is not the stereoselective reaction.

The mathematical models for the initial stage of the thermal degradation of PVC which give the possibility to describe this process up to $\sim 30-40\%$ conversion, have been proposed. The mathematical models for the PVC degradation may be used for investigation of the initial stage of decomposition of a wide range of the polymers which degrade with the splitting out of side fragments from macromolecules [the Eq. (1)], such as poly(vinyl bromide), poly(vinyl fluoride), poly(vinyl acetate), poly(vinyl alcohol), *etc.*

Early [10, 11, 27, 29, 35] on the basis of the numerous experimental data it has been suggestted that the nonautocatalytic thermal degradation of PVC mostly proceeds by a molecular mechanism complicated by radical reactions. Recently [48, 65] the most probable reactions of initiation of PVC dehydrochlorination by the radical mechanism have been proposed.

The new theory that the autocatalytic thermal degradation of PVC is the branched chain reaction with the degenerated branching of chain was developed. The reactions with the participation of polyenes and polyenyl carbocations excited into the triplet state, make the principal contribution to the degenerated branching of chain. HCl shows as the catalyst of these reactions [the Eqs. (51), (53) and (54)] which proceed with the small rate in the nonautocatalytic thermal degradation of PVC also [the Eqs. (31)–(34)].

Acknowledgements

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