STATISTICAL MODEL OF DEHYDROCHLORINATION OF POLYVINYL CHLORIDE IN INERT ATMOSPHERE

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A statistical model of dehydrochlorination of PVC in inert atmosphere based on zip mechanism has been suggested. A good agreement has been found between experimental and theoretical curves of the dehydrochlorination carried out to high conversion degrees. Mathematical evaluation gives the activation energy and the frequency factor of the random splitting off of HCl from PVC: $E_a = 170$ kJ mol^{-1}, log $(A/s^{-1}) = 12.9$ (independent of the PVC type).

An undesirable property of polyvinyl chloride (PVC) is its low thermal stability. PVC is decomposed at enhanced temperatures, dehydrochlorination being almost the only reaction up to 250°C, which results in formation of polyene sequences in PVC chain. Mechanism of the thermal dehydrochlorination of PVC in inert atmosphere has been given considerable attention. The dehydrochlorination kinetics of its model compounds was studied in detail[1-7], and also there exist a number of reports dealing with experimental studies of PVC itself[8-18]. Attempts were made[19-23] to describe theoretically the kinetic curves of the PVC dehydrochlorination, but so far the problem has not been solved satisfactorily. In the present paper a statistical model of the PVC dehydrochlorination is suggested and used for theoretical analysis of kinetic curves of the dehydrochlorination carried out to high conversion degrees.

THEORETICAL

Model of the Dehydrochlorination Course

Comparison of kinetic parameters of the dehydrochlorination of PVC with those of its model compounds reveals that the activation energy of elimination of HCl from the model compounds with ideal structure of PVC chain (as *e.g.* 2,4,6-trichloroheptane[1]) is greater than the corresponding value of the PVC dehydrochlorination of model substances containing C=C bonds (as *e.g.* 3-chloro-1-butene, 4-chloro-2-pentene *etc.*[1]) showed that their dehydrochlorination activation energy is smaller than the activation energy of the model compounds with ideal structure of PVC chain.

Application of these findings to the PVC dehydrochlorination leads to a zip mechanism[11,24] whose validity is accepted in the present paper, too.

Suppose that the whole PVC sample is formed by a single polymer chain containing N monomer units. At the dehydrochlorination temperature some of the monomer units can attain randomly an energy equal to or greater than the activation energy (E_a) of the random splitting off of HCl from PVC chain. Probability of attaining such energy is considered equal for all units (inclusive of the dehydrochlorinated ones). If a non-dehydrochlorinated unit attains the activation energy, the activated complex is formed, and the dehydrochlorination reaction takes place. This model of the reaction mechanism does not take into account consecutive reactions after the dehydrochlorination, i.e. if a dehydrochlorinated monomer unit attains the activation energy, no kinetic process takes place. The energy increase of a monomer unit to or above the activation energy value is called activation of that unit, and activation of a monomer unit is called a reaction step.

It has already been stated that no splitting off of HCl takes place, if the activated monomer unit is a dehydrochlorinated one. The monomer unit adjacent to the formed isolated double bond is dehydrochlorinated faster, because the activation energy is lowered by the conjugation energy of the π-system being formed in the activated complex (conjugation with the already present C=C bond). This effect of a system of conjugated double bonds on dehydrochlorination of the adjacent monomer unit is called allyl catalysis. The allyl catalysis has the consequence that the dehydrochlorination of the monomer units adjacent to a system of conjugated double bonds goes on fast, the polyene system being lengthened. This reaction is called a zip growth, and the polyene sequences formed are usually called zips. The longer the double bond system formed by the dehydrochlorination, the lower the contribution of conjugation energy between this system and the π-system being formed in the activated complex. Hence, with increasing zip length the effect of the allyl catalysis decreases, and after reaching a certain length the zip is terminated, i.e. its growth ceases[24]. The symbol m denotes the average zip length for the PVC whose dehydrochlorination degree (x) approaches zero. After a certain time from the beginning of the PVC dehydrochlorination a dynamic equilibrium is attained between random formation of growing zips and their termination. From the point of view of this equilibrium, m represents the average number of the growing zips in a time interval between two random activations. As the m value is about ten[24], an approximation can be introduced which enables to derive a statistical kinetic equation of the PVC dehydrochlorination in inert atmosphere: it is pressumed that after a random formation of C=C bond the subsequent zip growth is instantaneous. The state of the PVC chain assessed by this approximation differs only negligibly from its real state, and the approximation will cause a systematic error only in very early stages of the dehydrochlorination before reaching of the above-mentioned dynamic equilibrium.

The Zip Number

If the activated monomer unit lies near some of the zips, the growing zip can attach itself with the original zip to form a single longer zip. During such a reaction step the number of the eliminated HCl molecules is lower than m. Hence, the average number of the eliminated HCl molecules per one reaction step depends on both the dehydrochlorination degree and number of the zips. Let us suppose that the total zip number in the PVC chain is z, and number of the reaction steps within a time t is n. After the first reaction step the PVC chain contains one zip. The second step can form either one or two zips. One zip is formed, if two zips are joined or the activated unit is a dehydrochlorinated one. Similarly for $n = 3$ the number of zips can be 1, 2 or 3, *i.e.* the number of zips is not equal to the number of the reaction steps.

In the terms of the suggested model of the PVC dehydrochlorination, one finished reaction step can either leave the zip number unchanged or can increase it by one or can decrease it by one, the last case taking place, if two zips are separated by only one monomer unit, and this unit is activated. Hence the zip number can be expressed as follows:

$$z = 1 + \sum_{i=2}^{n} q_i - \sum_{i=3}^{n} r_i ; \tag{1}$$

where q_i and r_i mean the probabilities that, during the i-th reaction step, the zip number will be increased or decreased, respectively.

For expressing the probability r_i it would be necessary to know distribution of lengths of non-dehydrochlorinated segments of the PVC chain and, therefrom, to find the number of the non-dehydrochlorinated segments having the length of 1 monomer unit. As this distribution is not known, we shall try to assess the zip number in another way. Let p be the probability that z will not increase during one reaction step. In the first approach let us presume that p is independent of the dehydrochlorination degree. From Fig. 1 it can be seen that *e.g.* for $n = 4$ the average zip number is

$$z = p^3 \cdot 1 + 3p^2q \cdot 2 + 3pq^2 \cdot 3 + q^3 \cdot 4 , \tag{2}$$

where $q = 1 - p$. By generalisation it is possible to derive the expression:

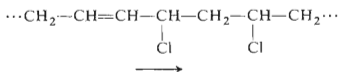$$z = \sum_{i=0}^{n-1} \binom{n-1}{i} p^{n-1-i} \cdot q^i \cdot (i+1) = p + nq . \tag{3}$$

If it is realized that n is a very great number, then

$$z = n \cdot q . \tag{4}$$

This relation represents a good approximation for calculation of z even when the probability p depends on x.

The Probability Expression

The probability p can be defined as the ratio of number of the monomer units which can be activated without increasing z to the total number of units. As the first units which can be activated without increasing z we can consider the dehydrochlorinated monomer units whose number is $N.x$. In an ideal PVC chain $...CH_2$—$CHCl$—CH_2—$CHCl$—CH_2—$CHCl...$, a random formation of $C=C$ bond bond will weaken the adjacent β—C—Cl bond[24], and, therefore, the zip will grow in the following direction (see the arrow):

$$\cdots CH_2\!-\!CH\!=\!CH\!-\!CH\!-\!CH_2\!-\!CH\!-\!CH_2\cdots$$
$$\quad\quad\quad\quad\quad\quad | \quad\quad\quad\quad | $$
$$\quad\quad\quad\quad\quad\quad Cl \quad\quad\quad Cl$$
$$\quad\quad\quad\quad\quad\underrightarrow{\quad\quad}$$

The zip number will not be increased, if a zip is joined with another one, i.e. if one to m units at the left-hand side of the zip or one unit at the right-hand side of the zip are activated. Number of such monomer units is equal to $(m + 1) z$ in a PVC chain whose dehydrochlorination degree is $x \to 0$.

Let us suppose that the PVC chain is dehydrochlorinated in the following way:

$$\boxed{}\!-\!\boxed{\ m\ }\!-\!\overset{m'}{\cdots}\!-\!\boxed{\ m\ }\!-\!\boxed{}$$
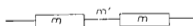
(the dehydrochlorinated and non-dehydrochlorinated segments with m and m' units respectively). Obviously, if $m' < m$, then some of the monomer units are involved two times in the sum $(m + 1) z + Nx$, because the regions $(m + 1) z$ and Nx are partially overlapped. For calculation of this overlap it would again be

FIG. 1

Diagram of relation of total average zip number (z) and number of reaction steps (n). The numbers in rule borders denote the possible number of zips
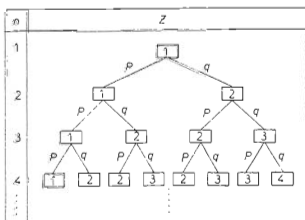
necessary to know distribution of lengths of the non-dehydrochlorinated segments of the PVC chain. This distribution being not known, we shall try to assess the overlap P. For $x \to 0$ distances between the zips are great and $P \to 0$. For $x \to 1$ the zips are close to each other, being separated by one non-dehydrochlorinated monomer unit only, and, hence, $P \to zm$. The overlap is assessed by the linear relation $P = zmx$, fulfilling the mentioned limit conditions. The probability p can be expressed by Eq. (5) whose combination with Eq. (4) gives Eq. (6).

$$p = (Nx + z(M + 1) - zmx)/N \tag{5}$$

$$z = n(1 - x)/(1 + n(1 + m(1 - x))/N) \tag{6}$$

Kinetic Equation of the Dehydrochlorination

Number of the HCl molecules eliminated from the PVC chain in one reaction step depends on position of the activation. Let u_i be the activation probability of a monomer unit at a certain position of the PVC chain, d_i meaning number of the HCl molecules eliminated in connection with the given activation position.

i) If the activated monomer unit lies in a dehydrochlorinated segment of the PVC chain, then no HCl molecules are eliminated, *i.e.* $d_1 = 0$. The activation probability of the unit in this PVC segment is $u_1 = Nx/N = x$.

ii) Let us suppose that the activated monomer unit lies in the vicinity of a zip (described in the previous part). If the overlap is taken into account, then 1 to $m(1 - x)$ HCl molecules can be eliminated from the left-hand side of the zip, and one HCl molecule can be eliminated from the right-hand side. Having denoted $j = m(1 - x)$, the average number of the molecules eliminated on activation in the neighbourhood of a zip will be

$$d_2 = \frac{1 + 2 + 3 + \ldots + j + 1}{j + 1} = \frac{\frac{1}{2}j(j + 1) + 1}{j + 1} = \frac{m(1 - x)}{2} + \frac{1}{1 + m(1 - x)} \tag{7}$$

The activation probability of the monomer unit of this PVC segment is $u_2 = z(1 + m(1 - x))/N$.

iii) If the activated monomer unit lies in some of other parts of the PVC chain, then $d_3 = m$ HCl molecules are eliminated with the probability $u_3 = (N - Nx - z(1 + m(1 - x)))/N$.

Average number h_n of the HCl molecules eliminated in the n-th reaction step can be expressed by Eq. (8).

$$h_n = \sum_{i=1}^{3} u_i d_i = \frac{z(1 + m(1 - x))}{N} \left[\frac{1}{1 + m(1 - x)} + \frac{m(1 - x)}{2} \right] +$$

$$+ \frac{N - Nx - z(1 + m(1 - x))}{N} m . \tag{8}$$

Combination of Eqs (6) and (8) leads to Eq. (9).

$$h_n = (1 - x) \left\{ m - \frac{\frac{n}{N}(1 + m(1 - x))}{1 + \frac{n}{N}(1 + m(1 - x))} \left[m - \frac{1}{1 + m(1 - x)} - \frac{m(1 - x)}{2} \right] \right\} . \tag{9}$$

The aim of our attempts is to find number of the HCl molecules eliminated in all the reaction steps, *i.e.* expression for the sum

$$h = \sum_{n=1}^{n_0} h_n , \tag{10}$$

where n_0 means number of the reaction steps during the time interval we are interested in. As n_0 represents a very large number, the sum can be replaced by the integral. Assuming $x = h/N$, it is

$$x = \int_1^{n_0} (1 - x) \left\{ m - \frac{\frac{n}{N}(1 + m(1 - x))}{1 + \frac{n}{N}(1 + m(1 - x))} \right.$$

$$\left. \left[m - \frac{1}{1 + m(1 - x)} - \frac{m(1 - x)}{2} \right] \right\} \frac{dn}{N} . \tag{11}$$

At a certain moment, number of monomer units with energy equal to or greater than the activation energy is given by some of the energy distribution laws, and therefore, number of random activation per time unit is a function of temperature only. At a constant temperature it is thus $n/N = Bt$, where B means constant of proportionality. If the first reaction step is presumed to take place at the time $t = 0$,

then Eq. (11) is transformed into:

$$x = \int_0^{t_0} B(1 - x) \left\{ m - \frac{Bt(1 + m(1 - x))}{1 + Bt(1 + m(1 - x))} \cdot \right.$$
$$\left. \cdot \left[m - \frac{1}{1 + m(1 - x)} - \frac{m(1 - x)}{2} \right] \right\} dt \tag{12}$$

or taking the derivative with respect to time:

$$dx/dt = B(m - s)(1 - x), \tag{13a}$$

where

$$s = \frac{Bt(1 + m(1 - x))}{1 + Bt(1 + m(1 - x))} \left(m - \frac{1}{1 + m(1 - x)} - \frac{m(1 - x)}{2} \right). \tag{13b}$$

It can be easily shown that

$$\lim_{t \to 0} s = 0 \, . \quad \lim_{\substack{t \to \infty \\ (x \to 1)}} s = m - 1 \, . \tag{14a,b}$$

According to Eq. $(13a)$ the PVC dehydrochlorination in inert atmosphere represents formally a first order reaction with the rate constant $k_{eff} = B(m - s)$. As it can be seen from Eqs $(13a)$ and $(14a)$ for the early stages of dehydrochlorination it is $k_{eff} = Bm$. This expression for the rate constant agrees with that derived in ref.[23].

In final stages of the dehydrochlorination the zips are very close to each other, hence for $x \to 1$ one HCl molecule will only be eliminated on activation of a non-dehydrochlorinated monomer unit. In this way, the zip mechanism of dehydrochlorination changes into random elimination of HCl from PVC chain. Combination of Eqs $(13a)$ and $(14b)$ reveals that in final phases the PVC dehydrochlorination obeys the relation

$$dx/dt = B(1 - x). \tag{15}$$

This relation also reveals physical meaning of the constant of proportionality B: it is the rate constant of random elimination of HCl from PVC chain.

Formal Kinetic Equation of PVC *Dehydrochlorination*

In this section the kinetic equation of dehydrochlorination of PVC is derived with the use of an approach analogous to that of ref.[23]. It is presumed that after random formation of an isolated C=C bond the zip grows at a certain rate and the growth is finished after attaining a certain zip length. In accordance with the paper by Minsker

and coworkers[21], the random elimination of HCl from the PVC chain is called initiation reaction, the growth of the zip is called propagation reaction, the last phase being called termination reaction. The corresponding rate constants are k_i, k_p, and k_t. We will limit ourselves to the early stages of dehydrochlorination only.

The process of formation of the growing zips can be described by Eq. (16a), where $[g_z]$ means concentration of the growing zips in the PVC chain.

$$d[g_z]/dt = k_i(1 - x) - k_t[g_z] . \qquad (16a)$$

After a certain time interval from the beginning of the dehydrochlorination a dynamic equilibrium is established between formation and termination of the growing zips, which can be expressed mathematically as $d[g_z]/dt = 0$, or

$$[g_z] = k_i(1 - x)/k_t . \qquad (16b)$$

The rate of the PVC dehydrochlorination can be expressed by Eq. (17a) which, on substitution from Eq. (16b), gives Eq. (17b).

$$dx/dt = k_i(1 - x) + k_p[g_z] \qquad (17a)$$

$$dx/dt = k_i(1 + (k_p/k_t))(1 - x) \qquad (17b)$$

Eq. (17b) represents kinetic equation of the 1. order with the effective rate constant

$$k_{eff} = k_i(1 + (k_p/k_t)) . \qquad (18)$$

In the previous section it was shown that $B = k_i$. By comparison of the relation $k_{eff} = Bm$ with Eq. (18) it can be found $m = 1 + (k_p/k_t)$. As the rate constants should fulfil the Arrhenius equation, the equations $\log B = f(1/T)$ and $\log(m - 1) = f(1/T)$ should be linear.

RESULTS

Simulation of Kinetic Curves of PVC Dehydrochlorination in Inert Atmosphere

For testing the statistical model of the PVC dehydrochlorination in inert atmosphere we used the data of refs[16-18]. According to Eq. (13a) the kinetic curves of time dependence of the dehydrochlorination degree (at a given temperature T) depend parametrically on B and m. The differential equation (13a) cannot be separated, and, therefore, it was solved numerically by the Runge–Kutta method[25]. The non-

-linear least squares method was used for comparison of the theoretical and experimental curves. The sums of squares of deviations between the experimental and theoretical degrees of dehydrochlorination were minimized for selected time intervals by the simplex method[26].

For the temperatures $200-220°C$ the kinetic curves were measured to relatively low degrees of dehydrochlorination (about 0.3). In this range of x the factor s (Eq. *(13b)*) has a small value, and, therefore, Eq. *(13a)* is degenerated to the form $dx/dt = Bm(1 - x)$. In this case the condition of the minimum sum of the deviation squares is fulfilled best by any combination of the B and m parameters fulfilling the relation $k_{eff} = Bm$. Also for $x < 0.6$ the minimum of sum of squares of deviation is flat and corresponds to a fairly broad interval of the B and m parameters. Due to these reasons, the Arrhenius dependences cannot give any information.

The above-mentioned difficulties were circumvented by simultaneous simulation of a whole set of the experimental curves given in some of refs[16−18]. This procedure is based on the Arrhenius dependences of the form:

$$B = A \cdot \exp\left(-E_a/RT\right), \quad m = 1 + \Delta A \cdot \exp\left(-\Delta E_a/RT\right), \qquad (19a,b)$$

where A and E_a mean the frequency factor and the activation energy, respectively, of the random elimination of HCl from PVC, and ΔA and ΔE_a mean ratio of the frequency factors and difference of the activation energies, respectively, corresponding to the rate constants k_p and k_i; R stands for the gas constant. In this case we minimized the sum of squares of deviations between the experimental and the theoretical x values for the whole set of curves, the variation parameters being A, E_a, ΔA, and ΔE_a.

TABLE I

Values of kinetic parameters A, E_a, ΔA, ΔE_a and x_m corresponding to the minimum sum of the deviation squares

Set	$\log(A/s^{-1})$	E_a, kJ mol^{-1}	$\Delta \log(A/s^{-1})$	ΔE_a, kJ mol^{-1}	x_m	Ref.
	12·92	172·9	−4·69	−51·7	—	16
A	12·94	171·3	−4·47	−44·0	—	17
	12·94	174·0	−4·53	−50·8	—	18
	12·93	170·7	−4·26	−45·6	0·910	16
B	12·53	166·6	−4·45	−42·5	1·000	17
	12·92	168·7	−4·09	−40·9	0·849	18

Table I, set A gives values of the parameters A, E_a, ΔA, and ΔE_a fulfilling the condition of the least sum of deviation squares, and Fig. 2a gives theoretical curves for data of ref.[16]. From the figure it can be seen that there is a considerable discrepancy between the experimental and the theoretical curves especially at higher x values, the theoretical x values being higher than the experimental ones. A similar discrepancy was found between the experimental and theoretical curves corresponding to data of ref.[18]. This fact can easily be explained by impossibility of the PVC dehydrochlorination to be carried out up to $x = 1$ (due to the presence of impurities etc.). Therefore, we carried out another minimization according to the parameters A, E_a, ΔA, ΔE_a and x_m, where x_m means the maximum possible dehydrochlorination degree.

After introduction of the x_m parameter it is necessary to modify the derivation of the kinetic equation ($13a$) of the PVC dehydrochlorination. In this case the overlap P is assessed by the relation $P = zmx/x_m$. The probability p is expressed by Eq. (20)

$$p = \left(N(1 - x_m) + Nx + z(m + 1) - (zmx/x_m)\right)/N \qquad (20)$$

and introduction of this relation into Eq. (4) results in Eq. (21).

$$z = n(x_m - x)\Bigg/\left(1 + \frac{n}{N}\left(1 + m\left(1 - \frac{x}{x_m}\right)\right)\right). \qquad (21)$$
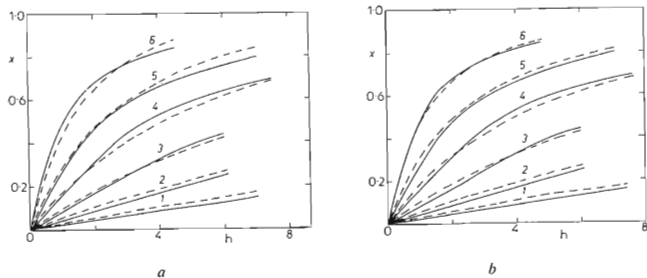

FIG. 2

Experimental (———) and theoretical (-----) curves of PVC dehydrochlorination in inert atmosphere for ref.[16]. Temperatures (°C): 1 200, 2 210, 3 220, 4 230, 5 240, 6 250 (a) The variation parameters A, E_a, ΔA, and ΔE_a; (b) the variation parameters A, E_a, ΔA, ΔE_a, and x_m

The probabilities u_2 and u_3 are given by the relations:

$$u_2 = z(1 + m(1 - (x/x_m)))/N , \tag{22a}$$

$$u_3 = (N - Nx - N(1 - x_m) - z(1 + m(1 - (x/x_m))))/N , \tag{22b}$$

and the corresponding numbers of the eliminated HCl molecules from the PVC chain are:

$$d_2 = \frac{1}{1 + m(1 - x/x_m)} - \frac{m(1 - x/x_m)}{2} , \quad d_3 = m . \tag{23a,b}$$

Repeating the above-described derivation of kinetic equation of dehydrochlorination we can obtain Eq. (24).

$$\frac{dx}{dt} = B(x_m - x)\left\{m - \frac{Bt(1 + m(1 - x/x_m))}{1 + Bt(1 + m(1 - x/x_m))} \cdot \right.$$
$$\left. \cdot \left(m - \frac{1}{1 + m(1 - x/x_m)} - \frac{m(1 - x/x_m)}{2}\right)\right\} . \tag{24}$$

The theoretical kinetic curves involving the x_m parameter are given in Fig. 2b (for data of ref.[16]). It can be seen that the experimental and theoretical curves of dehydrochlorination show an improved agreement. Similar results were obtained also for the kinetic curves published in ref.[18]. In the case of the kinetic curves published in ref.[17], for which it is $x_m = 1$, the difference between the kinetic parameters given in Table I (cf. the Sets A and B) is due to inaccuracy of the calculation method. The maximum difference between the experimental and theoretical x values is 0·035, the average difference being less than 0·02. The parameters A, E_a, ΔA, ΔE_a, and x_m corresponding to the minimum of sum of the deviation squares are given in Table I, Set B.

Kinetic Parameters of Random Elimination of HCl from PVC

From Table I it can be seen that both the activation energy and frequency factor of the random elimination of HCl from PVC are practically identical for all the types of PVC studied in refs[16-18]. These values vary within the limits $E_a = 166·6 \div 174·0$ kJ mol^{-1}, $\log (A/s^{-1}) = 12·53 \div 12·94$. The individual PVC sorts only differ in their ΔA and ΔE_a values, i.e. the average zip length (at a given temperature) will be different for different PVC types. This quantity depends, inter alia, on tacticity of the polymer chain[27]. On the contrary, the kinetic parameters of random elimination of HCl from the PVC chain appear to be characteristic properties of vinyl chloride monomer unit, being negligibly influenced by the chain structure, which is indicated by agreement of A and E_a parameters of different PVC types.

In our opinion, this distinct agreement between the kinetic parameters of the random elimination of HCl from PVC can be generalized in the conclusion that the activation energy of the random elimination of HCl from PVC is $E_a = 170 \text{ kJ mol}^{-1}$, and the frequency factor is $\log(A/\text{s}^{-1}) = 12.9$, and the both values are independent of the PVC type. The mentioned values are only slightly higher than those obtained by Troitskii and coworkers[19] by a different method ($E_a = 159.1 \pm 4.2 \text{ kJ mol}^{-1}$, $\log(A/\text{s}^{-1}) = 11.8 \pm 0.5$).

Temperature Dependence of m and z

From Eq. (*19b*) it follows that the average zip length depends on temperature (Fig. 3). It is seen that the m value decreases with increasing temperature. This fact can be explained as follows: For the allyl catalysis to operate it is inevitable that the π-electron system of the conjugated bonds causing the allyl catalysis is coplanar with the π-electron system being formed in the activated complex of the PVC dehydrochlorination. Increasing temperature increases intensity of thermal motions of the monomer units, which results in deviation of the activated complex from the plane of the π-electrons. *i.e.* the conjugation between the activated complex and the π-system is disturbed. The action of the thermal motion of the monomer units results in a diminished effect of the allyl catalysis at higher temperatures and, hence, in formation of shorter zips, which was observed by Thallmaier and Braun[28] during investigation of samples of PVC powder.

The average zip length m is closely connected with number of zips. Fig. 4 gives the function $z = z(x)$ for the data[16]. At higher temperatures more zips of shorter length are formed than at lower temperature. The functions $z = z(x)$ for various temperatures show a maximum which is due to joining of zips. These dependences show similar course for data of refs[17,18]. The temperature dependences of m and z were obtained from the data of Table I, Set B.
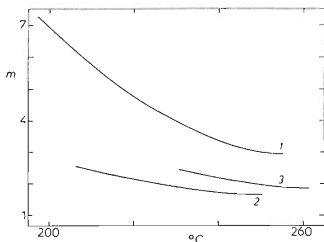
Fig. 3

Temperature dependence of the average zip length (m): 1 ref.[16], 2 ref.[17], 3 ref.[18]

Difference between Kinetic Parameters of PVC *Dehydrochlorination and those of the Model Substances*

From Eq. (18) it is easily possible to derive the relations for effective activation energy E_{eff} and effective frequency factor of the PVC dehydrochlorination A_{eff}:

$$E_{eff} = E_a + \frac{\Delta E_a}{1 + 1/(m + 1)}, \quad A_{eff} = Am \exp\left(\Delta E_a / RT\left(1 + \frac{1}{m - 1}\right)\right) \quad (25a,b)$$

With the use of the values of Table I it can be seen that the effective frequency factor for the PVC types studied in refs[16-18] lies in the interval $10^{9.4} \div 10^{11.4}$ s^{-1}, and the effective activation energy lies within the interval $130 \div 150$ kJ mol^{-1}, which agrees very well with the values found experimentally. From this result it follows that Eq. (18) makes it possible to explain the decrease of the measured frequency factor values and activation energy values of the PVC dehydrochlorination as compared with the corresponding kinetic parameters of dehydrochlorination of the model substances having ideal structure of the PVC chain. The mentioned decrease is due to the fact that the PVC dehydrochlorination is no elementary reaction but a kinetic process composed of several consecutive reactions.

DISCUSSION

The suggested statistical model of the PVC dehydrochlorination in inert atmosphere takes into account asymmetrical influence of the allyl catalysis on the dehydrochlorination of a monomer unit adjacent to polyene sequences. The advantage of the model lies in that it is not necessary to know the distribution of the zip lengths, it is sufficient to know their overall number. Also the role played by the labile structures in the PVC dehydrochlorination is neglected, because an only small amount of these
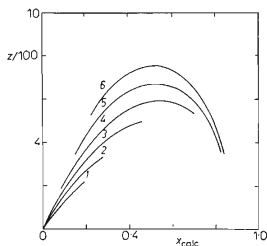

Fig. 4

Dependence of zip number per 100 monomer units ($z/100$) on theoretical dehydrochlorination degree ($x_{calc.}$) and temperature for ref.[16] Temperature (°C): *1* 200, *2* 210, *3* 220, *4* 230, *5* 240, *6* 250

groups is present in PVC, and, therefore, they can cause elimination of an only negligible part of HCl in kinetic measurements of the dehydrochlorinations carried out to high conversion degrees. This simplified approach enables a theoretical description of kinetic curves of the PVC dehydrochlorination within the whole range of the measured conversion degrees.

The weakest point of the suggested model is in its approximation of the dependence of zip number on the number of the reaction steps (Eq. (4)). On the basis of the results obtained it is possible to suppose that Eq. (4) represents a good assessment for calculation of the zip number. A more detailed analysis can show that the kinetic parameters of the random elimination of HCl from PVC are not affected by this approximation and can be considered to be correct, being also only slightly changed on going from Eq. $(13a)$ to Eq. (24). Only the values of ΔA and ΔE_a parameters are affected which are in a way transformed and can only be used for qualitative considerations[29].

Another drawback of the model suggested lies in that the number of the eliminated HCl molecules (d_2) exhibits a minimum $(d_2)_{min} = 0.914$ for $x = 1 - 0.414/m$. It is obvious that the minimum should have been $(d_2)_{min} = 1$ for $x = 1$. This deficiency is probably due to the not very good assessment of the overlap $(P = zmx)$.

In spite of the said imperfections the suggested model appears to be suitable for investigation of the kinetic curves of the PVC dehydrochlorination carried out up to high conversion degree. It can be presumed that an analogous model will be derived for the PVC dehydrochlorination in various atmospheres or for elimination of low-molecular compounds from vinyl and vinylidene type polymers.

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