Irregular Structures in Poly(vinyl chloride). I. Saturated Structures

[a]L. VALKO, [b]I. TVAROŠKA, and [a]V. KELLÖ

[a]*Institute of Physical Chemistry, Slovak Technical University, Bratislava 1*

[b]*Institute of Chemistry, Slovak Academy of Sciences, Bratislava 9*

In the present communication, consideration of the mechanism of dehydrochlorination of PVC is mainly described on the basis of information summarized from model-compounds studies. The semiempirical method proposed by *Vedeneyev* was used to study the C—Cl, C—H, and C—C bonds in poly(vinyl chloride). Activation energies for elimination of hydrogen chloride were calculated on the principle of the additivity of bond energies of the four-centre activated complex, for various saturated abnormal structures in the polymer molecule, such as branching, and head-to-head or tail-to-tail addition. Branched structures having a tertiary chlorine appear to have a significant effect upon initiation of thermal dehydrochlorination. The results of activation energies calculated empirically for particular saturated structures show that the tendency of C—Cl cleavage depends on the electronegativity of carbon bonded chlorine.

The thermal degradation of poly(vinyl chloride) (PVC) has attracted considerable attention over a fairly long period because of the wide industrial application of the polymer and its inherent instability. When exposed to various forms of energy PVC liberates hydrogen chloride to leave a highly coloured product. In certain circumstances cross-linking and chain-scission reactions can also occur with corresponding changes in the mechanical properties of the polymer but the word "degradation" tends to be confined to the dehydrochlorination reactions. The problem of PVC degradation has been tackled by many workers and has been the subject of several reviews [1—5] but there remains considerable controversy about the basic dehydrochlorination mechanism quite apart from the details of subsidiary reactions. In PVC thermal destruction the predominant reaction is the elimination of hydrogen chloride. No matter what the detailed mechanism may be, however, it is clear that the progressive elimination of hydrogen chloride from sequences of adjacent structural units is most readily initiated at various abnormal structures in the polymer molecule. Polymerization conditions, isolation, and storage contribute to irregularities such as chain-end group, branch points, random unsaturation, oxidation structures and extraneous impurities [6—8]. Most authors accept the view that dehydrochlorination takes place in the course of a zip-reaction, which means that the hydrogen chloride molecules are splitting off one after the other from monomeric units of the polymer; there are, however, different views relating to the starting step, the mechanism, and the length of the zip.

Despite numerous investigations on the thermal dehydrochlorination of PVC, the mechanism of this reaction is still poorly understood. In the literature, the mechanism of the process has been assumed to be radical [9—12], ionic [13—16] and unimolecular [17—23]. Despite the diversity of proposed mechanisms, there is common agreement that the idealized structure of $PVC—(CH_2—CHCl)_n—$, is intrinsically stable at temperatures below 200°C as confirmed by the thermal stability of model compounds such as 2,4-dichloropentane, 2,4,6-trichloroheptane, etc. [6, 24—27]. Thus instability in PVC must be caused by the structural abnormalities which are present to varying extents in all types of PVC. As yet little advance has been made in correlating dehydrochlorination with these structural irregularities mainly because of difficulties associated with complete characterization of PVC sample, a prerequisite for direct comparison of results from different laboratories.

The question to what extent the structural irregularities are involved in the dehydrochlorination of PVC would best be answered by a study of the kinetics of dehydrochlorination of model compounds, i.e., compounds containing one possible irregularity together with a sort chain of PVC. In the previous paper [27] the thermal stability of model compounds containing secondary and tertiary chlorine as well as unsaturated models corresponding to abnormal structures in PVC have been studied. In conjunction with the observation that the dehydrochlorination obeys a first-order rate law, an intramolecular process with a cyclic transition state is considered. Activation energies for elimination of hydrogen chloride were calculated on the principle of the additivity of bond energies of the activated complex for model compounds having various structural irregularities.

In the present communication consideration of the mechanism of dehydrochlorination of PVC is mainly described on the basis of information summarized from model-compounds studies [27]. We suppose that this treatment should ultimately give results of accuracy sufficient for prediction of reactivities of abnormal structures in PVC. The work described in this and in the following paper is a continuation of that in paper [27], devoted to elucidation of the mechanism of the dehydrochlorination reactions of PVC with particular reference to the reactivities of all kinds of abnormal structures present in the polymer chain.

In the present paper we deal only with problems of the mechanism of elementary reactions taking place in the course of the saturated abnormal structures degradation.

Estimation of dissociation energies of $C—C$, $C—Cl$, and $C—H$ bonds

Bond energies provide one of the simplest and most useful methods for the correlation of known heats of reaction and for the prediction of unknown heats and activation energies of reaction. Usually a constant energy is ascribed to each kind of bond. For example the carbon—carbon single bond is assumed to have the same energy in all molecules, or at least in all molecules in which each carbon atom is linked by single bonds to four other atoms. It has long been known that, in fact, bond energies are not fixed, but have different values in different molecules [28]. Furthermore, bond energy is one of the most fundamental properties of the chemical bond, and these deviations from constancy indicate significant deficiencies in valence bond theory.

Several equations for calculating bond-dissociation energies have been reported. A simple equation permitting calculation of bond-dissociation energies with remarkable degree of accuracy was deduced empirically by *Vedeneyev* [29]. The Soviet authors interpret the differences in the dissociation energies of particular bond on the basis of

Glockler's theorem [30], taking into consideration the energy resulting from the stabilization of the electron system of the resulting radicals. This energy is named joining energy by Semenov Glockler's reorganization energy, which additively influences the bond energy.

The dissociation energy Q_{R-X}, of a bond in a molecule $R-X$, can be expressed as follows

$$Q_{R-X} = E'_{R-X} - (B_R + B_X),\qquad(1)$$

where E'_{R-X} is the specific energy for a given type of bond, *i.e.*, $C-H$, $C-Cl$, and $C-C$, *etc.*, and where B_R and B_X are the stabilization energies of the radicals R and X, respectively. In the case when X represents an atom, then $B_X = 0$. In general, B_R and B_X can be calculated by a relationship given by the equation

$$B_R = \sum_{m,i} M_i\,\alpha_i \exp(-\omega\,m) + aE_{conj},\qquad(2)$$

where M_i is the number of bonds of the type i which are bonded with the m-th carbon from the bond under consideration, α_i is the specific parameter of the stabilization due to a given bond type, and $\exp(-\omega)$ is a coefficient independent of the type of bond in the molecule and having the value 0.4 found from experimental data of bond dissociation energies. In the last equation, a is the number of conjugated groups adjacent to the bond under consideration and E_{conj} is the stabilization energy imparted to a free radical by a conjugated group. The general expression for the dissociation energy, Q_{R-X} of bond in a molecule is

$$Q_{R-X} = E'_{R-X} - [\sum_{m,i} M_i\,\alpha_i \exp(-\omega\,m) + aE_{conj}] -$$
$$- [\sum_{n,j} N_j\,\alpha_j \exp(-\omega\,n) + bE_{conj}].\qquad(3)$$

Table 1

Values of the constants in Vedeneyev's equation

Constant	Value*
$\exp(-\omega)$	0.4
α_{C-H}	10.0
α_{C-Cl}	9.8**
α_π	11.0
E'_{C-H}	127.8
E'_{C-Cl}	109.3
E'_{C-C}	145.5
$E_{conj.}$	19.4

* All energetic parameters are expressed in kcal mole^{-1}.

** By using the bond dissociation energy, $Q_{CH_2Cl-H} = 98$ kcal mole^{-1} [29], the α_{C-Cl} value was determined as $Q_{CH_2Cl-H} = E'_{C-H} - \alpha_{C-Cl} - 2\alpha_{C-H}$.

Values of the E'_{R-X} and E_{conj} parameters, determined from experimental data on the dissociation energies of the bonds in simple hydrocarbons, are shown in Table 1. The values of bond dissociation energies, calculated by Vedeneyev's equation for relatively

complicated hydrocarbons, are in agreement with the observed values within about 3 kcal mole^{-1}.

Hence, it seems to be reasonable to apply Vedeneyev's semiempirical method to calculate the dissociation energies of C$-$Cl, C$-$H, and C$-$C bonds in PVC. For this estimate the assumption has to be made that the bond energies given by Vedeneyev's equation (3) applied to the solid state of PVC.

Activation energies

Modern reaction rate theory reduces the most ordinary problems in reaction rates to the problems in molecular structure and the potential of interaction between molecules. Specifically, according to the theory of absolute reaction rates as formulated by *Eyring* [31], the rate constant is given by equation (4)

$$k(T) = e \, \varkappa(\boldsymbol{k} \, T/\boldsymbol{h}) \exp(\varDelta S^{\text{+}}/\boldsymbol{R}) \exp(-E/\boldsymbol{R}T), \tag{4}$$

where the factor $\varkappa$ is known as the transmission coefficient, $(\boldsymbol{k} \, T/\boldsymbol{h})$ is a universal frequency dependent only on temperature and independent of the nature of the reactants and the type of reaction, $\varDelta S^{\text{+}}$ is the entropy of activation and E is the energy of activation. The main problems in calculating reaction rates are (i) calculation of the entropy of activation and (ii) calculation of the energy of activation. This is the part of reaction rate theory which has caused the most trouble.

The activation energy must be calculated quantum mechanically, estimated semiempirically or empirically, or determined experimentally. Neither strict quantum mechanical methods nor the *Eyring—Polanyi* semiempirical method [32] can at present be fruitful for solving the activation energy problem, in view of the difficulties involved and the large number of reactions of interest. An empirical but very successful method was devised by *Moin* [33].

It has been already established that a sigma electron system may usually be regarded as consisting of a localized bond model. This idea seems to be supported by the fact that many molecular quantities such as heats of formation, dipole moments and polarizabilities may be derived by means of bond additivity rules. On the other hand, there are some deviations from the additivity of bond properties due to delocalization effects. Moin extends the picture of the additivity of bond energies to the active bonds in activated complex configuration. The activation energy, E, per mole at absolute zero, is defined as follows

$$E = \sum_i Q_{\boldsymbol{i}} - \sum_i Q_i^{\text{+}} \tag{5}$$

$$\text{(cleavage bonds)} \quad \text{(active bonds)}$$

Various forms for the activated complex of reaction may be postulated and the activation energy estimated for each of them. It is known, however, that the rates of chemical reactions are influenced by the interactions of non-bonded atoms in the transition state. Contributions from the interactions of non-bonded atoms are not especially included in equation (5). We note that quantum mechanical calculations of the interactions of adjacent bond, which is equivalent to interactions of pairs of non-bonded atoms, is very significant for the determination of bond dissociation energies as pointed out by *Wiener* [34] and *Bernstein* [35].

According to Eyring's theory of rate processes, the rate of a reaction is given by the velocity at which the activated complex travels over the top of the potential barrier.

By analogy of model compounds, the mechanism of dehydrochlorination of PVC can be deduced to be the ionic molecular elimination that was suggested by *Imoto* and *Ota* [36]. For calculational purposes, following *O'Neal* and *Benson* [37], four-centre transition states have been represented in terms of one-electron bonds, as illustrated for idealized structure of PVC

$$\sim\!-CH_2\!-\!CHCl\!-\!CH_2\!-\!CHCl\!-\!\sim\; \rightleftarrows\; \sim\!-CH_2\!-\!\begin{bmatrix}\overset{\delta+}{\underset{\cdot}{-CH}}\!\!-\!\!\overset{\delta-}{\underset{\cdot}{CH}}\!-\\[2pt] \underset{\delta-}{Cl}\quad\underset{\delta+}{H}\end{bmatrix}^{\ddagger}\!\!-CHCl\!-\!\sim\; \rightleftarrows$$

$$\rightleftarrows\; \sim\!-CH_2\!-\!CH\!=\!CH\!-\!CHCl\!-\!\sim$$
$$Cl\overset{+}{-}H.$$
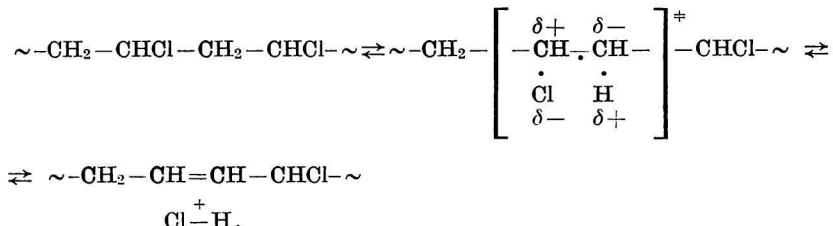
The longer distances pictured between the reacting H and Cl atoms are meant to imply that the interactions at these points are relatively weak. Thus, the transition states employed in the calculations are pictured as strongly polarized species which differ from the linear conformations by the weak interactions at the reacting ends. They therefore may be termed very loose cyclic structures. During the dehydrochlorination, one of C—Cl and C—H bonds are broken and one C—C-π and H—Cl bonds are formed. Thus, the activation energy for the elimination of hydrogen chloride at 0 K is

$$E = Q_{C\text{-}Cl} + Q_{C\text{-}H} - (Q_{C\text{-}Cl}^{\ddagger} + Q_{C\text{-}H}^{\ddagger} + Q_{\pi\text{-}C\text{-}C}^{\ddagger} + Q_{H\text{-}Cl}^{\ddagger} + \omega^{\ddagger}), \qquad (6)$$

where $\omega^{\ddagger}$ is parameter which is zero for saturated hydrocarbons and has different values for unsaturated compounds with the double bond located inside the chain $\omega^{\ddagger} = \beta_{C=C}^{\ddagger}$ and at the end of the chain $\omega^{\ddagger} = \alpha_{C=C}^{\ddagger}$.

The energy of activation determined experimentally E_{exp} is practically the same as the activation energy E in equation (5), the two differing essentially by RT for unimolecular gas reactions and for reactions in solution where the standard states are unit concentrations. Strictly the quantity E in equation (5) is more correctly defined as the microscopic activation energy which, at not too high temperatures differs little from the ex-

Table 2

Average values of active bond dissociation energies at 0 K

Type of bond		Active bond energy* $[Q^{\ddagger}$ kcal mole$^{-1}]$
C_p—Cl	primary chlorine	19.5
C_s—Cl	secondary chlorine	21.3
C_t—Cl	tertiary chlorine	24.5
σ-C—C	in saturated hydrocarbons	28.0
π-C—C	in unsaturated hydrocarbons	17.0
H—Cl	hydrogen chloride	40.0
$\alpha_{C=C}^{\ddagger}$	correction to the double bond located at the end of the chain	−17.0
$\beta_{C=C}^{\ddagger}$	correction to the double bond located inside the chain	−3.8

* Average values of active bond dissociation energies and correction parameters are calculated from model compounds studies [27].

perimentally determined activation energy. This is obtained in practice from the Arrhenius plot of the observed values of ln k against $1/T$. *Moin* [33] found empirically the active bond dissociation energies with remarkable accuracy from inspection of the great number of experimentally determined activation energies. The dissociation energies of the active bonds in simple hydrocarbons are shown in Table 2. The dissociation energy $Q_{C-H}^{\pm}$ of the C—H active bond for particular hydrocarbons was calculated by the equation [38]

$$Q_{C-H}^{\pm} = 0.83(Q_{R-H} - 45) \text{ kcal mole}^{-1}. \tag{7}$$

The values of the constants in Vedeneyev's equation and the average values of active bond dissociation energies, together with the parameter in the treatment, are listed in Tables 1 and 2. We have tested the above set of bond energy parameters (Tables 1 and 2) by comparing the calculated and observed activation energies of a number of saturated and unsaturated model compounds of PVC; the agreement is satisfactory.

The thermal stability of PVC is largely dependent on the polymerization process; so this effect should be discussed from the basic standpoint, relating to the species and location of abnormal structures.

Tail-head and tail-tail structure

There are two possible orientations of chlorine atoms in a molecule of PVC, namely, tail-head type and tail-tail type or in haphazard order. The former is conventionally designated as 1,3-polymer and the latter 1,2-polymer. A random polymer is defined usually as a mixture of these two types. While neglecting the end group effect, and supposing that chlorine reacts only with hydrogen on neighbouring carbons, and that no rings form in the course of reaction, the following schemes can satisfactorily explain the mechanism of this dehydrochlorination. The main reaction can be expressed as follows

If there is only one chlorine atom in each structural unit in the saturated chain, dehydrochlorination would give conjugated double bonds. However, in case there were two or more chlorines in a structural unit, an appreciable number of triple bond would also be formed.

The rate-controlling process in thermal dehydrochlorination of PVC is the initiation step, having a relatively high activation energy compared with that of other processes. We consider 1,3-polymer as the idealized structure of PVC formed by head-to-tail addition. The following numbering of bonds is used

$$\sim -CH_2-CHCl-CH_2-CHCl-\overset{1}{C}H-CH-CH_2-CHCl-CH_2-\sim \tag{A}$$

We shall use the following notation convention: Q_i ($i = 1, 2, 3, \ldots$), defined by equation (3), represents the C—H or C—Cl bond dissociation energy of bond i, Q_j' ($j = 1, 2, 3, \ldots$), defined by equation (3), represents the C—C bond dissociation energy of bond j, and E_k ($k = I, II, III, \ldots$), defined by equation (6), represents activation energy of the possible four-centre transition state complex k, formed by individual

8

C—H and C—Cl bonds. The four-centre structures are designated by the solid or by the dotted square, respectively. The structural parameters used in these calculations are summarized in Tables 1 and 2. The calculation yields the following bond dissociation energies and activation energies*

$$Q_1 = 91.36, \quad Q_2 = 72.74, \quad Q'_1 = 79.08, \quad E_I = 47.32.$$

The 1,2-dichloride structure, corresponding to a tail-to-tail configuration (B), formed by the termination reaction should be considered to be a more stable structure than the

$$\sim\!-\text{CH}\!-\!\text{CH}\!-\!\text{CH}\!-\!\text{CH}\!-\!\text{CH}\!-\!\text{CH}\!\cdot\ +\ \cdot\text{CH}\!-\!\text{CH}\!-\!\text{CH}\!-\!\text{CH}\!-\!\sim$$

(B)

$$\rightarrow\ \sim\!-\text{CH}\!-\!\text{CH}\!-\!\text{CH}\!-\!\text{CH}\!-\!\text{CH}\!-\!\text{CH}\!-\!\text{CH}\!-\!\text{CH}\!-\!\text{CH}\!-\!\text{CH}\!-\!\sim$$

I   II   III   IV
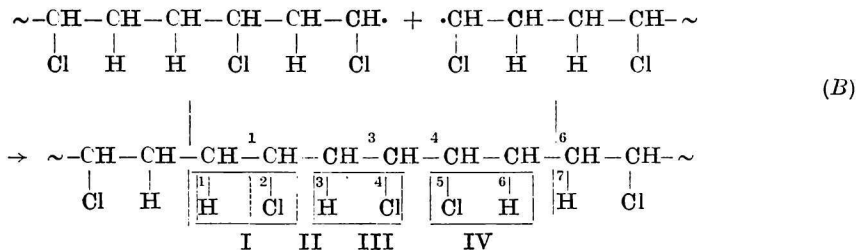
normal one which has a secondary chlorine, according to the results of the study of chloroalkanes of low molecular weight by *Erbe et al.* [39] and the thermal stability of vinyl chloride-*trans*-dichloroethylene copolymer reported by *Kitamura* and co-workers [40]. Generally, the structure (B) represents a random polymer. As in the case of 1,3-polymer, it is assumed that hydrogen condenses only with neighbouring chlorines. By referring to *Flory*'s expression [41] a molecule of random polymer of infinitely long chain may usually be divided into groups of structural units as shown above.

The portion between the vertical lines is 1,4-linkage with respect to the consecutive structural units and contains one 1,2-linkage, and undetermined number of 1,3-linkages and no 1,4-linkages. Accordingly, if the number of 1,3-linkages in a portion increases, this portion would bear a close resemblance in structure to a 1,3-polymer [42].

The calculated values for the random polymer are

$$Q_1 = 91.34 \quad Q_2 = 72.78 \quad Q_3 = 91.38 \quad Q_4 = 72.83 \quad Q_5 = 72.81 \quad Q_6 = 91.37 \quad Q_7 = 91.36$$

$$Q'_1 = 79.01 \quad Q'_2 = 79.04 \quad Q'_3 = 79.03 \quad Q'_4 = 79.14 \quad Q'_5 = 79.04 \quad Q'_6 = 78.90$$

$$E_I = 47.44 \quad E_{II} = 47.38 \quad E_{III} = 47.43 \quad E_{IV} = 47.41$$

Thermal stability of structures having primary chlorines (C), which would be formed by chain-transfer termination to the monomer or termination by disproportionation, is insignificant because this structure is highly stable if compared with secondary chlorines

$$\sim\!-\text{CH}_2\!-\!\text{CH}\!\cdot\ +\ \cdot\text{CH}\!-\!\text{CH}_2\!-\!\sim\ \rightarrow\ \sim\!-\text{CH}_2\!-\!\text{CHCl}\!-\!\text{CH}\!-\!\text{CH}\!-\!\text{CH}_2$$

(C)
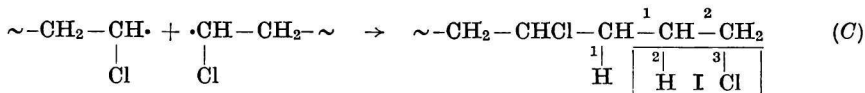
Q_i and E_i have values

$$Q_1 = 91.49 \quad Q_2 = 92.27 \quad Q_3 = 75.75$$

$$Q'_1 = 79.82 \quad Q'_2 = 81.89 \quad E_I = 52.40$$

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* All quantities are expressed in kcal mole^{-1}.

If all the chlorine atoms in PVC were secondary, the thermal stability of PVC should be maintained below 200°C. This was confirmed [27] by the thermal decomposition of model compounds such as 2,4-dichloropentane, 5,7-dichlorododecane and 2,4,6-trichloroheptane. Therefore, the instability of PVC could be related to the abnormal structures which could be varied by the conditions of polymerization. The most unstable C—Cl bonds are allyl chlorines, distributed at random over the polymer chain, and tertiary chlorines existing at the junction of branches that can be formed by chain-transfer reaction during polymerization process.

Branched structures

The chain-transfer reaction is significant especially in vinyl chloride polymerization, because through this reaction many undesirable irregular structures are produced at the surface of the precipitated particles. If this reaction occurs only by "backbiting", it is assumed that there is no relationship between the thermal stability of PVC and the conversion of polymerization. However, the thermal stability of PVC depends largely on the conversion of polymerization [43].

Tertiary chlorine atoms are also present in PVC as shown by the work of *Cotman* [44]. These branches structures are presumably formed by chain transfer between a growing radical and an already formed polymer molecule. Branched structures should be capable of initiating dehydrochlorination is generally supposed by many authors [45—48]. Branched structures can be reduced by preventing the chain-transfer reaction by the lowering of polymerization temperature.

Loss of hydrogen chloride is initiated at tertiary chlorine branch points, double bonds should appear at random in the chain on thermal degradation. *Lím* and *Kolinsky* [49] carried out the polymerization in 2,4-dichloropentane and 2,4,6-trichloroheptane to determine the chain-transfer constant by the usual kinetic theory based on the assumption of the stationary state. Experimental evidence indicates that the chain-transfer reaction most likely takes place with the hydrogen on the same carbon as the chlorine. Therefore, it would be expected that most of the branches in PVC are attached to the chain in a tertiary chlorine-type structure.
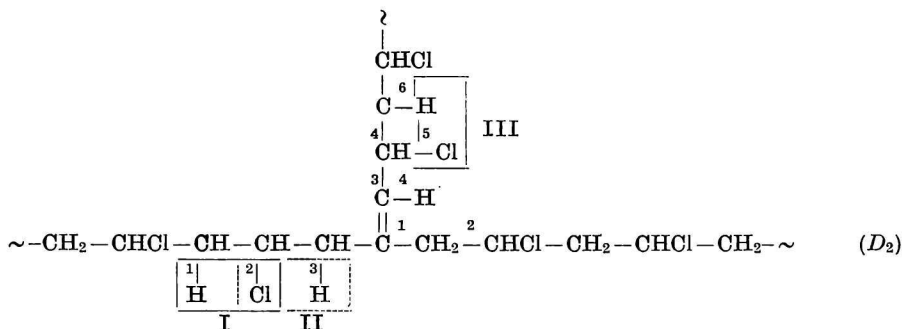
We consider (D_1) branched structure

$$
\begin{array}{c}
\wr \\
| \\
CH_2 \\
| \\
CHCl \\
| \\
CH_2 \\
| \ ^1 \quad ^2 \quad ^3 \\
\sim-CH_2-CHCl-CH_2-CHCl-CH_2-\overset{}{C}-\overset{}{CH}-CH-CH-CHCl-CH_2-CHCl-\sim \quad (D_1) \\
\end{array}
$$
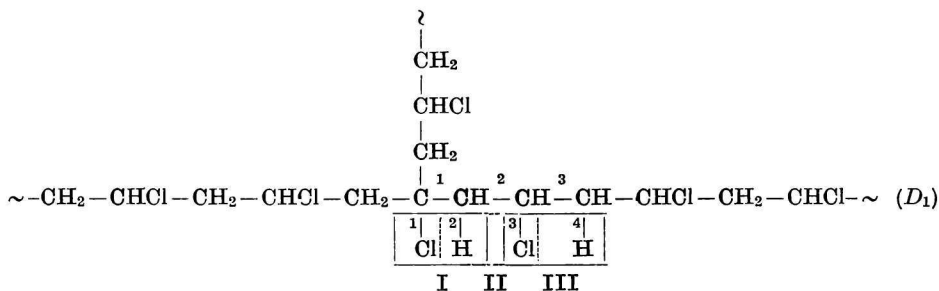
for which the calculated energetic parameters are

$$Q_1 = 69.91 \quad Q_2 = 90.41 \quad Q_3 = 72.62 \quad Q_4 = 91.53$$
$$Q_1' = 76.07 \quad Q_2' = 78.08 \quad Q_3' = 78.68$$
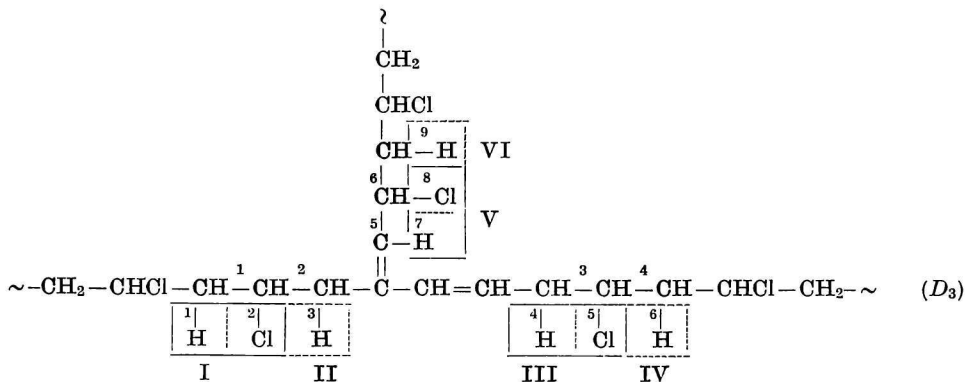$$E_I = 41.14 \quad E_{II} = 47.15 \quad E_{III} = 47.37$$

10

It is apparent from these data that hydrogen chloride is eliminated more readily from branched structures than from secondary chlorine atoms. The branched structure (D_1) is most unstable in all saturated abnormal structures as observed also from model compounds studies [27]. The first hydrogen chloride elimination from branched structure (D_1) is activated by only one tertiary C—Cl bond. After this first hydrogen chloride is lost, the next dehydrochlorination scheme (D_2) is said to involve one allylic activated site for elimination of hydrogen chloride

$$
\begin{array}{c}
\text{CHCl} \\
\text{C—H} \quad {}^{6} \\
\text{CH—Cl} \quad {}^{4} \; {}^{5} \quad \text{III} \\
\text{C—H} \quad {}^{3} \; {}^{4} \\
\sim\!-\mathrm{CH_2-CHCl-CH-CH-CH-C-CH_2-CHCl-CH_2-CHCl-CH_2-}\!\sim \\
\boxed{\text{H} \quad \text{Cl} \quad \text{H}} \\
\text{I} \qquad \text{II}
\end{array}
\qquad (D_2)
$$

The calculated values are

$Q_1 = 91.69 \quad Q_2 = 73.00 \quad Q_3 = 72.11 \quad Q_4 = 93.35 \quad Q_5 = 54.41 \quad Q_6 = 90.99$
$Q'_1 = 78.91 \quad Q'_2 = 59.75 \quad Q'_3 = 81.00 \quad Q'_4 = 60.57$
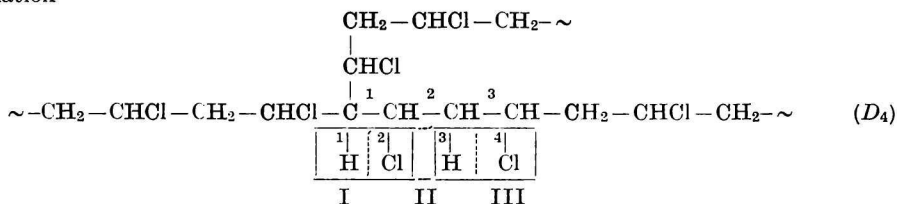$E_\mathrm{I} = 47.61 \quad E_\mathrm{II} = 44.33 \quad E_\mathrm{III} = 32.76$

Since hydrogen chloride can be lost in three directions from a branch point, we consider the following "zipper" structure (D_3) which is formed from the (D_1) by elimination of two molecules of hydrogen chloride. This dehydrochlorination structure has two allylic activated sites which accelerate the elimination of hydrogen chloride.

$$
\begin{array}{c}
\text{CH}_2 \\
\text{CHCl} \\
\text{CH—H} \quad {}^{9} \quad \text{VI} \\
\text{CH—Cl} \quad {}^{6} \; {}^{8} \\
\text{C—H} \quad {}^{5} \; {}^{7} \quad \text{V} \\
\sim\!-\mathrm{CH_2-CHCl-CH-CH-CH-C-CH=CH-CH-CH-CH-CHCl-CH_2-}\!\sim \\
\boxed{\text{H} \quad \text{Cl} \quad \text{H}} \qquad \boxed{\text{H} \quad \text{Cl} \quad \text{H}} \\
\text{I} \qquad \text{II} \qquad\qquad \text{III} \qquad \text{IV}
\end{array}
\qquad (D_3)
$$

The calculated energetic parameters are

$Q_1 = 91.74 \quad Q_2 = 73.49 \quad Q_3 = 72.67 \quad Q_4 = 73.43 \quad Q_5 = 73.48 \quad Q_6 = 91.28$
$Q_7 = 93.97 \quad Q_8 = 54.56 \quad Q_9 = 92.02$
$Q'_1 = 79.57 \quad Q'_2 = 60.22 \quad Q'_3 = 61.12 \quad Q'_4 = 79.99 \quad Q'_5 = 81.62 \quad Q'_6 = 60.88$
$E_\mathrm{I} = 48.15 \quad E_\mathrm{II} = 44.90 \quad E_\mathrm{III} = 44.93 \quad E_\mathrm{IV} = 48.08 \quad E_\mathrm{V} = 33.25 \quad E_\mathrm{VI} = 33.00$
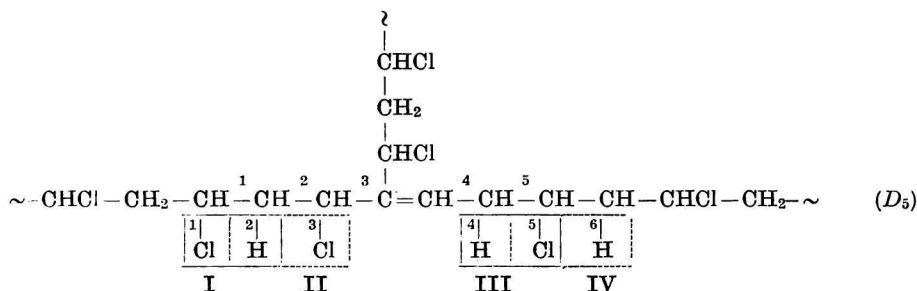
The branched structure (D_4) having a tertiary hydrogen at the junction of branches is formed by chain-transfer termination reaction to the methylenic carbon atom and not to the carbon atom directly bonded with chlorine atom. The branched structure (D_4) has also in this case an activating effect upon the first molecule of hydrogen chloride elimination

$$CH_2-CHCl-CH_2-\sim$$
$$|$$
$$CHCl$$
$$\underset{1}{|}$$
$$\sim-CH_2-CHCl-CH_2-CHCl-\overset{1}{C}-\overset{2}{CH}-\overset{3}{CH}-CH-CH_2-CHCl-CH_2-\sim \qquad (D_4)$$
$$\underset{\text{I}}{\underline{\overset{1|}{H} \, \overset{2|}{Cl}}} \quad \underset{\text{II}}{} \quad \underset{\text{III}}{\underline{\overset{3|}{H} \, \overset{4|}{Cl}}}$$

for which the calculated values are

$$Q_1 = 88.51 \quad Q_2 = 71.86 \quad Q_3 = 91.23 \quad Q_4 = 72.88$$
$$Q_1' = 76.14 \quad Q_2' = 78.11 \quad Q_3' = 78.88$$
$$E_I = 45.89 \quad E_{II} = 46.42 \quad E_{III} = 47.44$$

After the first hydrogen chloride elimination we have

$$\zeta$$
$$|$$
$$CHCl$$
$$|$$
$$CH_2$$
$$|$$
$$CHCl$$
$$\sim-CHCl-CH_2-\overset{1}{CH}-\overset{2}{CH}-\overset{3}{CH}-\overset{|}{C}=CH-\overset{4}{CH}-\overset{5}{CH}-CH-CHCl-CH_2-\sim \qquad (D_5)$$
$$\underset{\text{I}}{\underline{\overset{1|}{Cl} \, \overset{2|}{H}}} \quad \underset{\text{II}}{\underline{\overset{3|}{Cl}}} \qquad \underset{\text{III}}{\underline{\overset{4|}{H} \, \overset{5|}{Cl}}} \quad \underset{\text{IV}}{\underline{\overset{6|}{H}}}$$

The calculated values are

$$Q_1 = 73.08 \quad Q_2 = 91.73 \quad Q_3 = 53.61 \quad Q_4 = 72.95 \quad Q_5 = 73.42 \quad Q_6 = 92.03$$
$$Q_1' = 81.20 \quad Q_2' = 59.94 \quad Q_3' = 79.08 \quad Q_4' = 78.40 \quad Q_5' = 60.60$$
$$E_I = 47.78 \quad E_{II} = 32.11 \quad E_{III} = 44.89 \quad E_{IV} = 48.12$$

After these two molecules of hydrogen chloride are eliminated, the next labile allyl site structure (D_6) has two double bonds and two allylic activated sites which accelerate the elimination of hydrogen chloride. This structure is

$$\zeta$$
$$|$$
$$CH_2$$
$$|$$
$$CHCl$$
$$\overset{}{CH}\underline{\overset{8}{-H}}\, {}_{\text{IV}}$$
$$\underset{4|}{CH}\underline{-Cl}$$
$$\sim-CH_2-CHCl-\overset{1}{CH}-CH-C=CH-C=CH-\overset{2}{CH}-\overset{3}{CH}-CH-CHCl-CH_2-\sim \qquad (D_6)$$
$$\underset{\text{I}}{\underline{\overset{1|}{H} \, \overset{2|}{Cl}}} \quad \overset{3|}{H} \qquad \underset{\text{II}}{\underline{\overset{4|}{H} \, \overset{5|}{Cl}}} \quad \underset{\text{III}}{\underline{\overset{6|}{H}}}$$
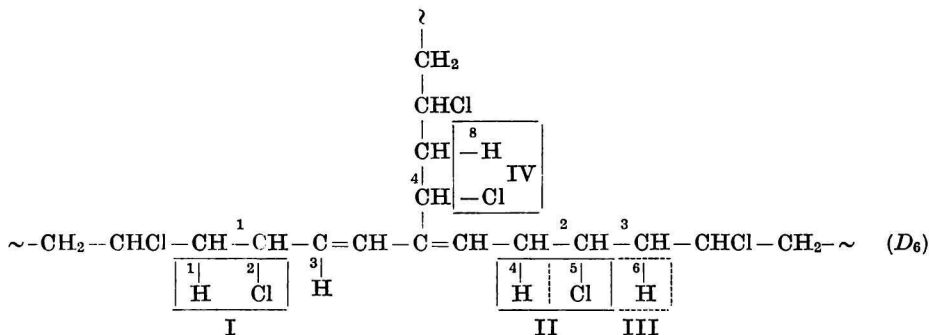
for which we have

$$Q_1 = 92.09 \quad Q_2 = 51.88 \quad Q_3 = 94.67 \quad Q_4 = 72.87$$
$$Q_5 = 73.41 \quad Q_6 = 91.81 \quad Q_7 = 54.00 \quad Q_8 = 91.91$$
$$Q_1' = 62.04 \quad Q_2' = 58.78 \quad Q_3' = 80.68 \quad Q_4' = 60.35$$
$$E_\text{I} = 30.56 \quad E_\text{II} = 44.88 \quad E_\text{III} = 47.99 \quad E_\text{IV} = 32.38$$

Discussion

The thermal dehydrochlorination of PVC, the degradation by elimination reactions has significant feature that, as a consequence of the degradation or of another reaction taking place in a monomeric unit, a product is formed which activates the neighbouring monomeric unit from the point of the process involved. The mechanism of this kind of dehydrochlorination has been pointed to be a sort of chain reaction, namely, a zip-reaction. Dehydrochlorination occurs first at random in the beginning to form unsaturated bonds at several arbitrary sites in the long polymeric chain and then the reactions proceed from these sites by zipping mechanism at a considerably high rate. If dehydrochlorination occurs in a zipping mechanism like a chain reaction, a long conjugated bond system should be formed easily.

In the experimental work of the rate of a thermally activated process, within the experimental accuracy, the rate of a given process can be described by equation (4). If in fact, the process occurs by the simultaneous operation of a number of mechanisms each of which has the same activation energy, then the equation (4) is correct. However, the same treatment could not be extended to cases where there are competing mechanisms of different activation energy. Mechanism is used here in a very general sense, to mean any reaction path by which the process can occur. And it is the purpose of this note to consider what physical interpretation can be given to the measured so-called frequency factor A_exp and activation energy E_exp values in such cases as is the dehydrochlorination mechanism of PVC. The thermal dehydrochlorination of PVC consisting of a set mechanism, not all of the same activation energy, we can define a distribution function $N(E)$ for these structural irregularities by making $N(E)\,\mathrm{d}E$ proportional to the number of structural defects available with activation energies between E and $E + \mathrm{d}E$ and to the factor appropriate to such structural irregularities.

Then, since A_exp and E_exp are found from a plot of experimental values of $\ln k$ against T^{-1}, we have [50]

$$E_\text{exp} = \frac{\int_0^\infty E\,N(E)\exp(-E/RT)\,\mathrm{d}E}{\int_0^\infty N(E)\exp(-E/RT)\,\mathrm{d}E} = -R\,\mathrm{d}(\ln k)\,\mathrm{d}(T^{-1}) \tag{8}$$

and

$$A_\text{exp} = N(E)\exp[(E_\text{exp} - E)/RT]\,\mathrm{d}E. \tag{9}$$

Clearly, it is impossible to derive the distribution function $N(E)$ from measurements of A_exp and E_exp only, but equations (8) and (9) do allow the evaluation of A_exp and E_exp for any given function $N(E)$. In this way, if other considerations suggest a possible form of distribution function, some of its parameters may be determined by measurements of A_exp and E_exp. The actual (measured) activation energy is an average quantity and depends on the shape of the distribution function $N(E)$ for defects in the polymer chains. In Table 3 there is given the energy of activation which arises from an Arrhenius equation with no pre-exponential temperature dependence.

Table 3

Activation energies for thermal dehydrochlorination of PVC

Polymer	Atmosphere	Activation energy [kcal mole^{-1}]	Ref.
emulsion	nitrogen	36.0	[53]
precipitated from cyclohexanone solution	nitrogen	36.5	[54]
PVC—azo	vacuum	26.0	[55]
PVC—γ	vacuum	30.0	[55]
PVC—BP	vacuum	32.0	[55]
PCU—G	nitrogen	36.0	[56]
SICRON	nitrogen	34.0	[57]
PEVIKON KL-2	nitrogen	31.0	[58]
suspension	in solution	30.0	[58]

Many of the gas-phase unimolecular reactions which have been studied appear to take place by way of four-centre cyclic activated complex. Most of the four-centre reactions are hydrogen halide elimination from the hydrocarbons to produce olefins [37].

For this estimate the assumption has to be made that dehydrochlorination occurs through the four-centre activated complex in the solid state of PVC. Q_i and Q'_j are the dissociation bond energies of reaction schemes $(A)-(D_6)$, and E_i are their activation energies obtained from estimated C—H and C—Cl bond energies. From our results it follows that the activation energies are always lower than the bond dissociation energies of the weakest bonds in the molecule structures $(A)-(D_6)$.

This is indication of concerted breaking and forming of bonds. Regardless of the structure of the remainder of the saturated and unsaturated compounds, consideration can be given to three forms when discussing the C—Cl bond: (i) R—Cl covalent, (ii) R$^+$—Cl$^-$ ionic, (iii) R$^-$=Cl$^+$ π-bonded. The conclusion is made that all the forms are important for the structures which have been studied.

Our results support the opinion that neither the idealized structure of PVC (A) nor the random polymer (B) is reason for the start of the thermal dehydrochlorination. The cause of thermal instability must therefore be sought elsewhere, for instance in the presence of the inherent weak links in the polymer chain. This concept is generally accepted as a reasonable consideration, because the thermal stability of model compounds having secondary chlorine, was intrinsically stable below 200°C. However, since the mechanism of thermal dehydrochlorination has been discussed from different standpoints, it can be concluded that hydrogen chloride is evolved from the sites of inherent instability in PVC, such as tertiary chlorine and allyl chlorine adjacent to carbon——carbon double bond, by a molecular four-centre transition state complex reaction. This mechanism is usually considered as an ionic reaction rather than a free radical reaction, but, definitely not the same reaction [43].

The irregular structures (A) and (B) having secondary chlorine showed higher activation energy than those having tertiary chlorine (D_1). It can be easily understood that the thermal stability of structure having primary chlorine (C) is insignificant because this structure is highly stable compared with structures of secondary and tertiary chlorine. These results are consistent with the well recognized fact that the tendency for

14

C—Cl cleavage depends upon the electronegativity of the carbon—chlorine, primary chlorine is more stable than secondary, and secondary is more stable than tertiary chlorine of a branched chain.

In principle, a variation in the bond polarity is accompanied by a change in the hybridization of the corresponding atomic orbital. In the absence of rigorous quantum-mechanical calculations, variations in the nature of the C—Cl σ-type bond are usually discussed in terms of changes in the hybridization of the relevant carbon atomic orbital very nearly of sp^3-type [51]

$$\Phi_C = (1/2)(\Phi_{2s} + \sqrt{3}\,\Phi_{2p\sigma}) \tag{10}$$

and in the ionic character of the bond. We assume that C—Cl bond can be expressed by a molecular wave function of the type

$$\Psi_{C-Cl} = N(\Phi_C + \lambda\Phi_{Cl}), \tag{11}$$

where N is a normalizing constant and Φ_{Cl} is a hybrid at the chlorine atom represented by

$$\Phi_{Cl} = \sin\alpha\,\Phi_{3s} - \cos\alpha\,\Phi_{3p\sigma} \tag{12}$$

and λ is a parameter to allow for the ionic character of the bond. The increasing polarities in the C—Cl bonds are caused not only by the increasing polarizability, but also by the increasing amount of $3s$ character in the hybrid orbitals (12). Using the symbol ϱ_{C-Cl} for the percent $3s$ character of the chlorine atomic orbital in the primary (p), secondary (s), and tertiary (t) C—Cl bond, it can be concluded that ϱ_{C-Cl} increases in the order, $\varrho_{C-Cl\,(p)} < \varrho_{C-Cl\,(s)} < \varrho_{C-Cl\,(t)}$. The dipole moments of this series also increase in going from primary to tertiary chlorine. The activation energies again decrease as the $3s$ character of the chlorine atomic orbital rises. The importance of polar factors in determining the energies of activation, a process involving the elimination of hydrogen chloride has been recognized [52]. The greatest decrease in activation energy occurs in the case of the branched structure (D_1). These variations in activation energies for random polymer and the regular head-to-tail structure are comparatively small and indicate that the polar properties of the C—Cl bond in these structures do not differ significantly.

More detailed calculations are needed to give an accurate picture of the electron densities induced in chloroalkanes and also in chloroalkenes by a substituent, and until these are known a quantitative analysis of the ground-state properties in terms of mesomeric and inductive parameters will not be possible. Mathematically, the magnitude of the inductive effect is given by the amount that the energy levels and wave functions of the hydrocarbon are changed by the potential field of the substituent. The substitution of chlorine acts in two ways, firstly by destroying the symmetry of any —(CH$_2$)— group into which the substituent enters, and secondly by a direct inductive effect of the chlorine atom. The concepts of inductive and resonance effects, both of which are related to electron migration, have proved to be useful in organic chemistry.

Because of its high electronegativity, chlorine attracts σ-electrons $(-I)$ and polarizes the C—Cl bond so that the C—Cl bond dipole attracts other electrons in the molecule towards the substituted carbon atom. The inductive effect is determined from the effect of the halogen on the properties of a saturated system.

The existence of tertiary chlorine in PVC and its importance for the ageing process of PVC is generally supposed by many authors [45—48]. *Baum* and *Wartman* [45] considered the sites for initiation of thermal decomposition of PVC to be unsaturated chain

ends at about 150°C and tertiary chlorine at 190°C. They considered the double bond at the chain end to be responsible for PVC instability although its concentration is less than supposed for tertiary chlorine. When tertiary chlorine is present in PVC it can initiate the decomposition reaction at lower temperatures than supposed [48].

To elucidate the role the tertiary chlorine plays in PVC stability, the reaction schemes (D_1) to (D_6) were studied. From our calculations it appears reasonable to conclude that the tertiary chlorine has a marked influence on PVC stability. The weak points which are considered as the initiators of the decomposition are the tertiary chlorine of the branched structures $(D_1)-(D_6)$ which exist in the main chain of PVC. These branched structures are presumably formed by chain transfer between a growing radical and an already formed polymer molecule. The first hydrogen chloride lost from the branched structure (D_1) is activated by only one tertiary C—Cl bond. After this first hydrogen chloride is lost, the generating labile allyl site is activated by one double bond. The increasing instability of this branched structure (D_2) compared to the simple saturated chain structures (A) to (C) may be responsible for the increasing hydrogen chloride elimination rate. The loss of each hydrogen chloride elimination from the polymer molecule forms a new labile site capable of further dehydrochlorination. Our calculations demonstrate the very different reactivities of branched structure (D_1) with the tertiary C—Cl bond and branched structure (D_4) with the tertiary C—H bond in elimination reactions. Evidently the presence of double bond in the polymer chain increases the probability of elimination reactions. One object of the following paper is to examine this evidence, and so to elucidate further the factors which determine the relative reactivities of the unsaturated structures.

References

1. Chevassus F., De Broutelles R., *The Stabilization of Polyvinyl Chloride.* Arnold, London, 1963.
2. Madorsky S. L., *Thermal Degradation of Organic Polymers.* Interscience, London, 1964.
3. Gordon G. Y., *Stabilization of Synthetic High Polymers.* Israel Program for Scientific Translations, Jerusalem, 1964.
4. Neiman M. B., *Ageing and Stabilization of Polymers.* Consultants Bureau, New York, 1965.
5. Jasching W., *Kunststoffe* **52**, 458 (1962).
6. Staundinger J. J. P., *Plast. Progr.* (London) **1953**, 9.
7. Rhys J. A., *Appl. Plast.* **4**, 47 (1961).
8. Rhys J. A., *Rubber Plast. Age* **44**, 261 (1963).
9. Barton D. H. R., Howlett K. E., *J. Chem. Soc.* **1949**, 155.
10. Bengough W. I., Sharpe H. M., *Makromol. Chem.* **66**, 45 (1963).
11. Fuchs V. W., Louis D., *Makromol. Chem.* **22**, 1 (1957).
12. Winkler D. E., *J. Polym. Sci.* **35**, 3 (1959).
13. Imoto M., Teyzin T., *Teijin Times* **28**, 8 (1958).
14. Baum B., *SPE J.* **17**, 71 (1961).
15. Rieche A., Grimm A., Mücke H., *Kunststoffe* **52**, 265 (1962).
16. Lo Scalzo E., *Mater. Plast. Elast.* **28**, 682 (1962).
17. Druesedow D., Gibbs C. F., *Nat. Bur. Stand. Circ.* **525**, 69 (1953).

18. Grassie N., *Chem. Ind.* **1954**, 161.
19. Boyer R. F., *J. Phys. Colloid Chem.* **51**, 80 (1947).
20. Talamini G., Cinque G., Palma G., *Mater. Plast. Elast.* **30**, 317 (1964).
21. Valko L., *J. Polym. Sci., Part C*, No. **16**, 1979 (1967).
22. Valko L., *J. Polym. Sci., Part C*, No. **16**, 545 (1967).
23. Braun D., Bender R. F., *Int. Conf. Chem. Transformation of Polymers*, Bratislava, June 1968
24. Asahina M., Ozonuka M., *J. Polym. Sci., Part A-2*, 3505, 3515 (1964).
25. Smith H. V., *Rubber Plast.* **4**, 47 (1961).
26. Chytrý V., Obereigner B., Lím D., *Int. Conf. Chem. Transformation of Polymers*, Bratislava, June 1968.
27. Valko L., Tvaroška I., *Eur. Polym. J.* **7**, 41 (1971).
28. Pauling L., *J. Amer. Chem. Soc.* **54**, 3570 (1932).
29. Vedeneyev V. I., Gurvich L. V., Kondratyev V. N., Medvedev V. A., Frankewich Ye. L., *Bond Energies, Ionization Potentials and Electron Affinities.* Arnold Publishers Ltd., London, 1966.
30. Glockler G., *J. Chem. Phys.* **56**, 289 (1952).
31. Glasstone S., Laidler K. J., Eyring H., *The Theory of Rate Processes*, p. 10. McGraw-Hill, New York, 1941.
32. Eyring H., Polanyi M., *Z. Phys. Chem.* **812**, 279 (1931).
33. Moin F. B., *Usp. Chim.* **7**, 1223 (1967).
34. Wiener H., *J. Amer. Chem. Soc.* **69**, 17 (1947).
35. Bernstein H. J., *J. Chem. Phys.* **20**, 263, 524, 1328 (1952).
36. Imoto M., Ota M., *Kogyo Kagaku Zasshi* **54**, 470 (1951).
37. O'Neal H. E., Benson S. W., *J. Phys. Chem.* **71**, 2903 (1967).
38. Semenov N. N., *Some Problems in Chemical Kinetics and Reactivity.* Princeton Univ. Press, Princeton—New Jersey, 1958.
39. Erbe F., Grewer Th., Wehage K., *Angew. Chem.* **74**, 988 (1962).
40. Kitamura R., Ureta M., Takeuchi T., *J. Appl. Polym. Sci.* **9**, 1669 (1965).
41. Flory P. J., *J. Amer. Chem. Soc.* **61**, 1518 (1939).
42. Tsuchida E., Shin C. N., Shinohara I., *J. Polym. Sci.* **B3**, 643 (1965).
43. Onozuka M., Asahina M., *J. Macromol. Sci. — Revs Macromol. Chem.* **C3**, 235 (1959).
44. Cotman J. D., Jr., *Ann. N. Y. Acad. Sci.* **57**, 417 (1953).
45. Baum B., Wartman L. H., *J. Polym. Sci.* **28**, 537 (1958).
46. Parker E., *Kunststoffe* **47**, 443 (1957).
47. Bengough W. I., Norrish R. G. W., *Proc. Roy Soc.* (London) **A200**, 301 (1950).
48. Caraculacu A. A., *J. Polym. Sci., Part A-1*, **4**, 1839 (1966).
49. Lím D., Kolínsky M., *J. Polym. Sci.* **53**, 173 (1961).
50. Nicholas J. F., *J. Chem. Phys.* **31**, 922 (1959).
51. Coulson C. A., *Valence.* Oxford University Press, London, 1952.
52. Valko L., Tvaroška I., to be published.
53. Scarbrough A. L., Kellner W. L., *Nat. Bur. Stand. Circ.* **525**, 95 (1953).
54. Michaylov N. V., Tokareva L. G., Klimenkov B. S., *Kolloid. Zh.* **18**, 597 (1956).
55. Stromberg R. R., Straus S., Achhammer B. G., *J. Polym. Sci.* **35**, 355 (1959).
56. Štepek J., Vymazal Z., Doležel B., *Symposium on Thermal Stability of Polymers*, Prague, 1960.
57. Talamini G., Pezzin G., *Makromol. Chem.* **39**, 26 (1960).
58. Lisý M., *Chem. Zvesti* **17**, 248 (1963).