THERMAL DEHYDROCHLORINATION OF POLY(VINYL CHLORIDE) IN SYNDIOTACTIC SYSTEMS*

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The thermal dehydrochlorination of syndiotactic poly(vinyl chloride) sequences has been studied theoretically on low-molecular weight models ranging from vinyl chloride dimer to pentamer using the semiempirical quantum chemical MNDO method. Parameters obtained with saturated systems and their change caused by the proceeding elimination of hydrogen chloride accompanied by the formation of the corresponding unsaturated structures are discussed with respect to the repeated chloroallyl or α-chloropolyene activation of the dehydrochlorination process. The study of the assumed radical and ionic intermediates is used in discussing the reaction mechanism of dehydrochlorination, and the radical or ionic mechanism is supposed to be operative depending on the reaction conditions.

The heat instability of poly(vinyl chloride) (PVC) is so pronounced that this polymer cannot be processed without the presence of thermal stabilizers. The fact that in the years 1988 – 89 various PVC products were used in more than 4 000 kinds of applications and PVC thus became the polymer most widely in use is mainly due to the empirical experience in the development and use of stabilizing systems. However, such commercial success of PVC is still lacking the corresponding theoretical knowledge of its thermal degradation and stabilization. The stabilizing systems used at present are based on the effect of metallic stabilizers, especially of organic salts of Ca, Ba, Pb, Zn and Sn compounds, which – bearing in mind the yearly worldwide production of PVC amounting to some 20 million tons – represent a real ecological problem. It seems evident, therefore, that any improvement in the knowledge of these problems is of importance from both the economic and ecological point of view.

An analysis of the present-day state of knowledge of the thermal degradation and stabilization of PVC reveals that the reason of the low heat resistance of this polymer should be sought in structural defects present in polymer chains[1,2]. These are mainly defects consisting of chloroallyl structures or structures containing a chlorine atom bound onto a tertiary carbon atom, which at the processing temperatures initiate the chain dehydrochlorination of structural PVC units. Basically,

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* Part III in the series Thermal Dehydrochlorination of Poly(vinyl chloride), Part II: cf. ref.[2]

the problem of heat instability of PVC can be solved in two main directions: (i) by polymerizing vinyl chloride under conditions, where the formation of defective structures is suppressed partly or completely, or by removing defective structures from the polymer produced by a chemical reaction, (ii) by using such additives (stabilizers) in the processing of PVC which at least temporarily terminate the initiating and/or already propagating dehydrochlorination sites. The solution according to (i) has brought positive results, but has not yet been applied, mainly for economic reasons. The solution according to (ii) still offers great possibilities in the development and application of more effective metallic and/or nonmetallic organic stabilizers. The latter solution in particular calls for a better understanding of the course of dehydrochlorination reaction.

Dehydrochlorination measurements of PVC and vinyl chloride copolymers do not provide information on details of the elimination of hydrogen chloride. Since vinyl chloride oligomers are difficult to obtain experimentally, this study is focussed on a theoretical investigation of their dehydrochlorination behaviour in the series ranging from dimer to pentamer, including a description of the behaviour of the already unsaturated products, radical or ionic intermediates. As the effect of tacticity of the polymer chain on its dehydrochlorination has been reported in the literature[3], syndiotactic models have been dealt with in this study.

RESULTS AND DISCUSSION

Model Systems

The compounds studied were 2-chloropropane (C_3H_7Cl), 2,4-dichloropentane ($C_5H_{10}Cl_2$, a model of vinyl chloride dimer), 2,4,6-trichloroheptane ($C_7H_{13}Cl_3$), 2,4,6,8-tetrachlorononane ($C_9H_{16}Cl_4$) and 2,4,6,8,10-pentachloroundecane (below only $C_{11}H_{13}Cl_5$ for this model of pentamer), and unsaturated compounds derived from them (formed by dehydrochlorination) with one to four conjugated double bonds. The model system C_n is a chemical compound with n carbon atoms having the structure of a chloro derivative of a saturated or unsaturated hydrocarbon arising by dehydrochlorination (basic systems), or the structure of a radical or cation arising by the splitting off of a chlorine particle in the form of a radical or anion. Thus, the assembly of systems C_n includes $n + \pi_m - 1$ models (π_m being the highest possible number of double bonds in the conjugation); in the case of C_{11}, unsaturated structures with one to four double bonds in the conjugation are denoted with *I*, *II*, *III*, *IV*, i.e. we have model systems $C_{11}H_{18}Cl_4$ (*I*), $C_{11}H_{17}Cl_3$ (*II*), $C_{11}H_{16}Cl_2$ (*III*) and $C_{11}H_{15}Cl$ (*IV*). The semiempirical MNDO method[4] was used in the study; these assemblies were first fully optimized in geometries, then Mulliken's population analyses were applied, and the individual energy levels determined.

In the following step the splitting-off of the chlorine particle was simulated, either from the second carbon atom of the saturated system, or in the case of the unsaturated chain from the α-position to the π-electron system. The splitting proceeded either in the radical form (homolytic splitting of the C–Cl bond) or in the form of the chloride anion (heterolytic splitting). The organic fragments taken for the investigation were again subjected to full optimization of the geometry.

Although 2-chloropropane represents a considerable structural anomaly with respect to the PVC chain, its investigation has been included in the series of vinyl chloride oligomers, because it indicates limits up to which edge effects on the chain may influence the quality of calculation of these homologs.

Elimination of Hydrogen Chloride

In the first part of this study we have examined the energy conditions in the gradual splitting off of the HCl molecule from the individual oligomeric systems C_5-C_{11},

$$\text{R—CHCl—CH}_2\text{—R}' \rightarrow \text{HCl} + \text{R—CH=CH—R}\,, \qquad (A)$$

where R, R′ denote edge parts of the chain which may but need not contain double bonds. The results are summarized in Table I. The first column in Table I suggests that the data obtained by the MNDO method do not allow us to regard the growth of the polyene structure as an exothermic process. The formation of each new double bond and its incorporation into the π-conjugated system of the chain is connected with the supply of a certain small quantity of energy – approximately 53 kJ mol^{-1}. At this point we should keep in mind that the calculations performed represent energy relations at 0 K. Since Eq. (*A*) describes a process with a positive entropy value (the disorder in the system increases), the entropic term of the Gibbs potential very soon prevails over the low reaction enthalpy value. Thus, the experimentally observed fact that the dehydrochlorination of PVC proceeds spontaneously with a rapid polyene growth is not surprising.

The energy levels of frontier orbitals, HOMO and LUMO, are given in Table II. By comparing the data obtained for saturated oligomers and the corresponding 2-ene derivatives, it can be seen that the differences between the two orbitals $\Delta e_{(\mathrm{LUMO\text{-}HOMO})}$ and their position in the energy spectrum e_{LUMO} and e_{HOMO} are very close in the homologic series, particularly in the systems C_7, C_9 and C_{11}, which suggests that their chemical and physical behaviour is comparatively close. The C_7 system with two conjugated double bonds is already too extreme; consequently, its electron spectrum (at least at the MNDO level) differs in part from the C_9 and C_{11} systems (Table II, column 4).

Table II suggests that the energy of the HOMO orbital increases with the extent of dehydrochlorination of $C_{11}H_{19}Cl_5$, i.e. during the transition to structure *IV*.

Since with increasing energy of HOMO the reactivity of the given molecule also increases, it is obvious that systems with a higher HOMO should be more reactive with respect to their dehydrochlorination.

A more detailed analysis of the frontier HOMO/LUMO orbitals provides justification for yet another finding, namely, the "vertical behaviour" of their eigenvalues*, i.e. that the dominant properties of the systems are characterized by the π-electron system. Such behaviour is related to the character of the corresponding molecular orbitals. The HOMO and LUMO of saturated systems have an σ-bonding and σ-antibonding character, respectively, which however gradually changes to the character of the π-orbitals. In systems with two and more double bonds, the π-bonding HOMO orbital or the π-antibonding LUMO orbital can already be unambiguously observed.

TABLE I

Energy balances of dehydrochlorination processes (*A*), (*B*), (*B'*)

System	Phase[a]	ΔE(A)	ΔE(B)	ΔE(B')
			eV	
C_3	1Cl → 0Cl	—	2·72	6·67
C_5	2Cl → 1Cl	0·59	2·65	6·65
	1Cl → 0Cl	—	2·64	5·69
C_7	3Cl → 2Cl	0·55	2·62	6·67
	2Cl → 1Cl	0·57	2·58	5·67
	1Cl → 0Cl	—	2·62	5·18
C_9	4Cl → 3Cl	0·55	2·63	6·69
	3Cl → 2Cl	0·53	0·56	5·68
	2Cl → 1Cl	0·56	2·57	5·51
	1Cl → 0Cl	—	2·64	4·88
C_{11}	5Cl → 4Cl	0·55	2·62	6·69
	4Cl → 3Cl	0·53	2·56	5·69
	3Cl → 2Cl	0·52	2·54	5·16
	2Cl → 1Cl	0·56	2·59	4·84
	1Cl → 0Cl	—	2·65	4·67

[a] Notation e.g. 4Cl → 3Cl corresponds to the transition of a system containing four chlorine atoms to a system with three chlorine atoms.

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* The term "vertical behaviour" denotes the similarity with respect to columns of the tabulated values, i.e. between systems with the same number of double bonds. The term "diagonal behaviour" denotes the similarity between systems with the same number of chlorine atoms on the chain.

Mulliken's analysis of the systems gave charge distributions on the individual atoms. A complex view of partial charges on carbon atoms can be seen in Figs 1, 2. Figure 1 shows the charge distribution on carbon atoms in systems $C_{11}H_{19}Cl_5$ and structures *I*–*IV* with 1–4 double bonds. Figure 2 demonstrates a comparison between systems C_3–C_{11} containing one residual chlorine atom. The distribution

TABLE II

Energy levels (in eV) of the frontier orbitals (LUMO/HOMO) of basic systems

System	Saturated chain	Number of double bounds			
		1	2	3	4
C_3	0·73 −12·03	— —	— —	— —	— —
C_5	0·50 −12·06	0·15 −10·20	— —	— —	— —
C_7	0·35 −12·08	0·04 −10·28	−0·31 −9·29	— —	— —
C_9	0·30 −12·11	0·02 −10·31	−0·39 −9·34	−0·58 −8·82	— —
C_{11}	0·28 −12·12	0·00 −10·32	−0·41 −9·37	−0·64 −8·86	−0·75 −8·53

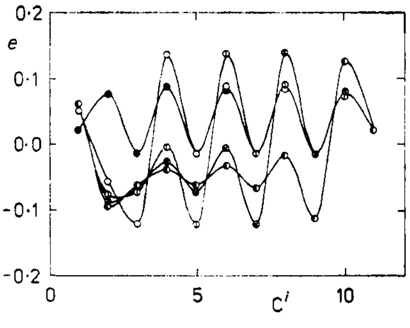

FIG. 1

Partial charge distribution on carbon atoms (C^i) of model systems C_{11}: ● $C_{11}H_{19}Cl_5$, ○ I, ⦶ II, ⊗ III, ◐ IV

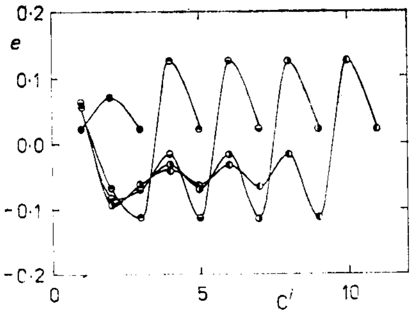

FIG. 2

Partial charge distribution on carbon atoms (C^i) of C_n systems containing the last uneliminated chlorine atom: ● C_3, ◓ C_5, ⊖ C_7, ◑ C_9, ◐ C_{11} (*IV*) of partial charges on carbon atoms in an unsaturated conjugated system should be a symmetrical function. Figure 1 suggested, however, that e.g. in a comparison of the magnitudes of edge minima, the calculated distributions are asymmetrical, which can be easily seen in the case of structure *IV*, where the second minimum of the negative partial charge (carbon atom C^9) is somewhat larger than the first minimum (carbon atom C^2). This finding is given by the chosen calculation model*. In this case, the more pronounced charge edge between carbon atoms C^9-C^{10} is connected with polarization of the carbon atom C^{10} due to the more electronegative chlorine atom, while the carbon atom C^1 binds three hydrogen atoms (methyl group). Hence, the slightly asymmetrical distribution of partial charges on the edge carbons atoms in a π-conjugated system is a consequence of different chemical surroundings.

The charge distribution on carbon atoms of the systems C_{11}, e.g. structures *III* and *IV* (Fig. 1), suggests the existence of the so-called charge resonance, i.e. the occurrence of maxima of the partial negative charge on the edge carbon atoms in the π-conjugated system. This finding supports a recent prediction[5] that the chain dehydrochlorination needs not proceed by the zip mechanism only, i.e. from the initiation site in one direction along the polymer chain, but that the polyene π-electron system may propagate alternately in both directions along the polymer chain.

After transition of the structure $C_{11}H_{19}Cl_5$ to structure *IV* the magnitude of the partial charge of chlorine atoms remains constant within the limits of error of the method used; also, the charge density of "important" hydrogen atoms remains unchanged**. This interesting finding is also illustrated in Figs. 1, 2. A change in the charge densities on chlorine or hydrogen atoms would necessarily be reflected in the magnitude of the maxima of the positive partial charge on the carbon atoms of the charge edges or on the following carbon atoms of the saturated systems, due to the different polarization. Figures 1, 2 show, however, that these values are approximately the same. Insignificant deviations are due to the existence of edge effects (cf. e. g. the difference between the charge edge of structures *III* and *IV*, Fig. 1). Figure 2 also indicates to what important extent the size of the given system affects the charge distribution of carbon atoms. It may be stated that already the

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* As it was necessary to make a compromise between the length of the calculated oligomers and the calculation requirements, it seemed more advantageous to eliminate molecules of hydrogen chloride gradually, starting from the 2nd and 3rd carbon atom, and to observe the effect of the propagating π-electron system on the relatively longer unperturbed chain, than to perform the first HCl elimination from the centre of the saturated system and face a possible complication caused by the edge effects of both chain ends. However, as can be seen in Fig. 2, these effects did not appear to be so significant.

** As "important" hydrogen atoms can be considered such hydrogens which are able to participate in the formation of the HCl molecule, such as hydrogen atoms on C^1 and C^5 carbon atoms of structure *II*, or on C^1 and C^7 carbon atoms of structure *III*, Fig. 1.

existence of two double bonds with the chlorine atom in the α-position gives a sufficiently exact description of the chloroallyl or α-chloropolyene activation.

At this point it is possible to answer the question regarding the nature of chloroallyl activation in terms of a molecular description. Using quantum chemical terms, it can be said that the chloroallyl activation is given by the existence of a charge edge between the end carbon atoms of the π-electron system and the starting saturated chain segment. This edge arises between the negatively charged carbon atom situated at the end of the π-electron conjugated system (C^{ω}), where the negative charge is cumulated, and the following carbon atom of the -CHCl- group (C^{α}) bearing a markedly positive partial charge. The magnitude of the charge potential, $\mu(C^{\omega} - C^{\alpha})$, is proportional to the strength used up by the system to remove this potential, or – in energy terms – it is proportional to a change in thermodynamic functions directed to the disappearance of this charge gradient. Another important finding, which can be derived from Fig. 1, concerns the magnitude of the charge edge potential $\mu(C^{\omega} - C^{\alpha})$. A comparison between systems dehydrochlorinated to various stages shows that with increasing π-electron conjugated system the magnitude of the $\mu(C^{\omega} - C^{\alpha})$ interaction remains unchanged within the limits of error of the MNDO method used.

Mechanism of Dehydrochlorination

In the second part of this study an attempt is made to elucidate the possible effect of chloroallyl activation on the propagation stage of dehydrochlorination, which proceeds in syndiotactic sequences of poly(vinyl chloride). First, the attention was focussed on the type of the mechanism, i.e. whether the dehydrochlorination proceeds via the radical or the ionic mechanism. For this purpose, the elimination of hydrogen chloride was divided into two reaction steps, viz., splitting off of the chlorine particle and completion of the HCl elimination by the subsequent elimination of the hydrogen atom. The first reaction step was simulated by the processes,

$$\mathrm{R{-}CHCl{-}CH_2{-}R'} \xrightarrow{-\mathrm{Cl}^{\bullet}} \mathrm{R{-}\dot{C}H{-}CH_2{-}R'} \qquad (B)$$

$$\mathrm{R{-}CHCl{-}CH_2{-}R'} \xrightarrow{-\mathrm{Cl}^{-}} \mathrm{R{-}\overset{(+)}{C}H{-}CH_2{-}R'} \qquad (B')$$

in which $\mathrm{R{-}CHCl{-}CH_2{-}R'}$ represents the individual saturated and unsaturated systems investigated in the first part of the study. The split-off chloride anion Cl^- was considered in its energetically more advantageous form HCl_2^-, the MNDO method gives preference to this form compared with the Cl^- anion ($E[HCl_2^-] - E[HCl] - E[Cl^-] = -1{\cdot}08$ eV). On the contrary, when considering the homolytic splitting of the C—Cl bond, we started from the radical form $Cl^{\bullet}$, which is energetically more advantageous ($E[HCl_2^{\bullet}] - E[HCl] - E[Cl^{\bullet}] = +0{\cdot}35$ eV).

The energy balance of processes (*B*) and (*B*′) is summarized in Table 1. Hence it can be seen that in the calculated systems modelling the isolated molecules, i.e. when no intra- or intermolecular interactions take place, the radical mechanism with the homolytic splitting of the C—Cl bond should predominate. Figure 3 shows to which extent the activation energy of splitting off of the chlorine particle depends on the number of conjugated double bonds in the system for both the radical and ionic mechanism. As these dependences are similar for all investigated systems, only assemblies of systems C_9 and systems C_{11} are demonstrated in Fig. 3. For the model structures chosen in this study, the activation energy of the radical mechanism is almost constant, not reflecting the number of conjugated double bonds in the systems (Fig. 3), and its value is roughly 250 $kJ\ mol^{-1}$. Unlike the radical mechanism, in the case of the ionic mechanism the activation energy is distinctly dependent on the length of the π-electron system. The shape of the curves suggests that there exists a limiting value of the activation energy of propagation of the polyene chain, to which a sufficiently long π-electron system converges. The dependence can be explained by assuming that the splitting off of each chloride anion may always show the same energy requirements, but – if the π-electron system is already existing – delocalization contributions may lead to a partial compensation of the activation energy. With increasing length of the conjugated system the relative role played by the delocalization energy gradually decreases, which explains the calculated trend of the ionic mechanism. Also, it can be seen from Fig. 3 that the activation energy of ionic splitting is markedly higher than that observed in the radical process. In view of the fact that with growing π-electron system the difference between the activation energies of the radical and ionic process decreases, the possibility that the radical mechanism of propagation of the polyene chain may be gradually replaced by the ionic mechanism may also be considered. In real systems, the extent of the ionic mechanism may be further extended due to various polar interactions, dissociation, and solvation effects. Thus, e.g., an experimental study of the dehydrochlorination of various unsaturated hydrocarbons containing the chlorine atom in the α-position with respect to the π-electron system has revealed[6,7] that with increasing number of double bonds the activation energy of the dehydrochlorination process decreases. The investigation of the cationic polymerization initiated with solid PVC has also led to a conclusion[8,9] that the formation of cationic propagation sites is probably a result of dipole-dipole interactions inside the polymer matrix.

The analysis of eigenvalues of the frontier orbitals is shown in Table III for the radical process and in Table IV for the ionic process of the chlorine particle elimination. If only higher oligomer systems C_7 through C_{11} are considered, a comparison between Tables III and IV reveals an important fact: Unlike ionic particles, the behaviour of intermediates of radical splitting after the elimination of the last chlorine atom (or if they contain one or two remaining chlorine atoms) is similar ("diagonal behaviour"). It can be said that in the simulation of the radical process, the predominant properties of the chain reflect the number of remaining chlorine substituents, which in turn is reflected in the agreement between the eigenvalues in the diagonal in Table III for the SOMO orbitals. The LUMO orbitals, similarly to both frontier orbitals in the case of the ionic mechanism, unambiguously reflect the length of the π-electron sequence. An analysis of the eigenvectors of the frontier orbitals provides

TABLE III

Energy levels (in eV) of the frontier orbitals (LUMO/SOMO/HDOMO) of radical intermediates

System	Elimination of chloride anion from carbon atom (C^i)				
	$Cl(C^2)$	$Cl(C^4)$	$Cl(C^6)$	$Cl(C^8)$	$Cl(C^{10})$
C_3	3·72	—	—	—	—
	−4·24	—	—	—	—
	−12·53	—	—	—	—
C_5	0·75	1·42	—	—	—
	−4·42	−4·31	—	—	—
	−12·98	−10·48	—	—	—
C_7	0·54	0·77	0·60	—	—
	−4·48	−4·42	−4·34	—	—
	−12·08	−10·28	−9·29	—	—
C_9	0·35	0·52	0·49	0·08	—
	−4·49	−4·47	−4·43	−4·37	—
	−12·11	−10·31	−9·34	−8·82	—
C_{11}	0·31	0·35	0·46	0·00	−0·26
	−4·50	−4·48	−4·46	−4·44	−4·38
	−12·07	−10·66	−9·66	−9·05	−8·60

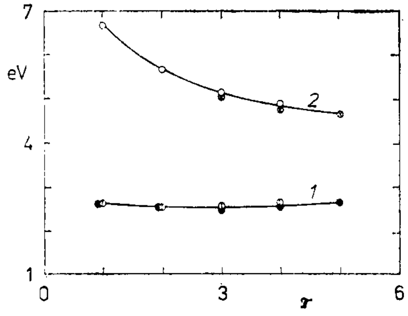

FIG. 3

Dependence of activation energy (in eV) on the number of conjugated double bonds (π) in C_9 and C_{11} systems: *1* radical mechanism, *2* ionic mechanism. *1* ⦶ C_9, ● C_{11}; *2* ○ C_9, ⊗ C_{11}

an explanation of such behaviour. HDOMO (Highest Double Occupied Molecular Orbital) and LUMO, respectively, are the orbitals in which the π-bonding and π-antibonding characters prevail. Unlike those, the SOMO orbitals are of the nonbonding type, containing only a part of carbon atoms of the π-electron system (inclusion of p_z orbitals after every other carbon atom). This analysis shows that the "vertical behaviour" of LUMO and HDOMO orbitals reflects the length of the π-electron polyene chain. The "diagonal behaviour" of SOMO radical assemblies is due to the fact that this is a nonbonding orbital occupied by a single electron. In the case of ionic splitting, the nonbonding character passes to the LUMO orbital, which because of being now vacant loses its "diagonal behaviour". It can be mentioned, moreover, that with respect to the molecular orbitals the difference between the frontier orbitals of the basic systems reported in the first part of this study (systems of nonradical and nonionic character), on the one hand, and these radical and ionic species on the other, consists in the introduction of the nonbonding orbital between the fully occupied bonding HOMO and the following antibonding orbital LUMO.

Tables III and IV show the nonmonotonic behaviour of the eigenvalues of HOMO ionic and LUMO radical systems. With the transition from saturated systems to

TABLE IV

Energy levels (in eV) of the frontier orbitals (LUMO-1/LUMO/HOMO) of cationic intermediates

System	Elimination of chloride ion from carbon atom (C^i)				
	Cl(C^2)	Cl(C^4)	Cl(C^6)	Cl(C^8)	Cl(C^{10})
C_3	−3·21	–	–	–	–
	−8·19	–	–	–	–
	−19·04	–	–	–	–
C_5	−3·71	−4·52	–	–	–
	−8·12	−7·39	–	–	–
	−16·29	−16·20	–	–	–
C_7	−3·81	−4·48	−4·35	–	–
	−8·15	−7·38	−6·88	–	–
	−14·89	−15·59	−14·37	–	–
C_9	−3·79	−4·50	−4·34	−4·29	–
	−8·16	−7·40	−6·88	−6·52	–
	−14·13	−14·53	−14·37	−13·23	–
C_{11}	−3·81	−4·51	−4·36	−4·29	−4·24
	−8·16	−7·40	−6·90	−6·53	−6·25
	−13·68	−13·90	−14·24	−13·24	−12·44

those with increasing polyene chain (e.g. system C_{11}, structure $C_{11}H_{19}Cl_5 \rightarrow IV$), the σ-bonding or the σ-antibonding character of the orbital in the given reaction intermediates changes to the corresponding π-character. In the case of HDOMO radical and LUMO ionic systems the same transition is connected with the existence of a maximum at the orbital energy values depending on the number of double bonds. A similar situation can be observed with the eigenvalues of HOMO and LUMO of the basic systems.

As it has been pointed out in the first part of this study, values of the energy levels of the frontier orbitals can be used to estimate reactivity of the systems. Tables III and IV suggest that the high eigenvalue of radical SOMO orbitals and the low LUMO energy values of ionic systems correspond to the considerable reactivity of both these types. The difference is caused by the fact that, due to its markedly low energy, LUMO of the ionic systems plays the role of electron acceptor, having the ability to accept the electron from higher energy levels of another particle. On the contrary, the radical system tends to recombine the unpaired electron from SOMO with the electron of a similar system with a simultaneous decrease in the energy of the occupied bonding molecular orbital and an increase in the energy of the vacant antibonding molecular orbital.

The resulting charge distributions on carbon atoms for the radical splitting of the C—Cl bond of C_{11} systems are demonstrated in Fig. 4. The individual curves suggest a change in the shape of the charge edge: the latter is now distributed among the three adjacent carbon atoms and not along the only one C—C bond. This is a direct consequence of the removal of the electronegative chlorine atom from the activation site and of the change of the partial charge on this carbon atom from positive to negative. The distributions indicate that the highest partial negative charge, and thus the largest charge gradient is formed in the case of splitting of the

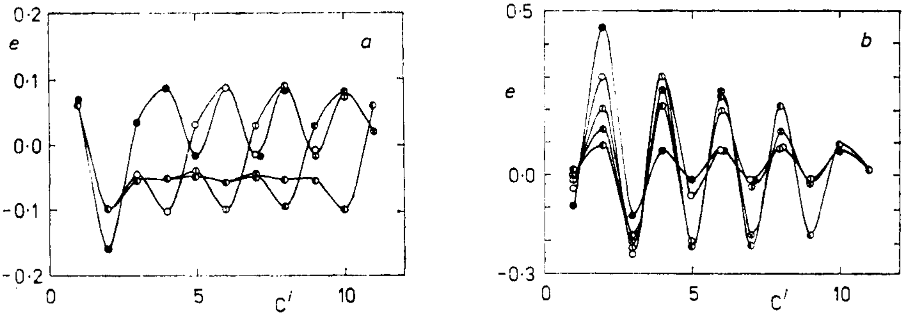

Fig. 4

Partial charge distribution on carbon atoms (C^i) of radical (a) and ionic (b) intermediates of C_{11} systems. (a) ● $C_{11}H_{19}Cl_4^{\bullet}$, ⊙ $C_{11}H_{18}Cl_3^{\bullet}$, ⦶ $C_{11}H_{17}Cl_2^{\bullet}$, ⊗ $C_{11}H_{16}Cl_4^{\bullet}$, ◐ $C_{11}H_{15}^{\bullet}$; (b) ● $C_{11}H_{19}Cl_4^-$, ⊙ $C_{11}H_{18}Cl_3^-$, ⦶ $C_{11}H_{17}Cl_2^-$, ⊗ $C_{11}H_{16}Cl^-$, ◐ $C_{11}H_{15}^-$

first chlorine particle. The formation of a larger gradient is connected with the existence of a relatively higher energy barrier, e.g. for the C_{11} system the activation energy for homolytic splitting of the first C—Cl bond, ΔE_1, is 2·62 eV (Table I). A comparison between distributions of the partial electron charge of structure *IV*, Figs 1 and 4, indicates the reason for the existence of a second higher barrier of homolytic splitting of the last chlorine particle, $\Delta E_5 = 2{\cdot}65$ eV, which however is related basically only to the model used. The charge edge of the α-chloropolyene activation is somewhat lower than in the cases of radical derivatives of $C_{11}H_{19}Cl_5$, *I*, *II*, *III*, which is reflected in its weaker efficiency. In other words, the homolytic splitting of the C^{10}—Cl bond requires a slightly larger amount of energy.

A comparison between charge distributions on carbon atoms of models *II*, *III* and *IV*, and of systems derived from them (Figs 1 and 4) shows that the homolytic splitting of C—Cl bonds does not cause large changes in the partial charge distribution on carbon atoms of the polyene sequence (Fig. 4*a*). In the case of ionic splitting the similarity of the partial charge distribution remains unchanged only in the unperturbed part of the chain (Fig. 4*b*). The lack of one electron causes pronounced alternations of the partial charge between positive and negative values with an approximate cumulation of the positive charge in the centre of the π-conjugated system. This is also an opposite feature compared with basic and radical intermediate systems, where the negative partial charge has been cumulated at the ends of the π-electron systems. Mulliken's population analysis makes possible a general explanation of energy balance trends of the C—Cl bonds ionic splitting (Table I, last column). It is obvious that for reasons similar to those used in discussing the charge edge, the formation of such considerable charge gradients will be connected with the existence of high energy states. This explains why the activation energy of ionic splitting is so high. Also, it is possible to extend the discussion concerning the dependence of activation energy on the number of double bonds. From a comparison of the charge distribution values on carbon atoms of ionic intermediates of *I*–*IV*, it can be seen that with growing polyene chain the difference in the oscillation of partial charges decreases, which probably reflects the decrease in activation energy mentioned above.

Figure 4 also shows that after the chlorine atom has been split off in the radical or anionic form, a π-electron system formed and its surroundings are almost symmetrical with respect to partial charges. This fact makes possible a subsequent splitting off of the hydrogen atom from carbon atoms in both α-positions to the conjugated system, with the same probability. This is also the main argument against a unilateral propagation starting from the initiation site and proceeding by a zip mechanism. In real systems, therefore, the polyenes should grow in the propagation stage of dehydrochlorination in both directions from the perturbation site.

An important finding obtained in the investigation of the chloroallyl (chloropropenylene) or α-chloropolyene activation is the fact that its driving force is caused by the existence of a charge potential $\mu(C^{\omega} - C^{\alpha})$. The results of the calculations show that this potential controls the formation of both polyenyl radicals and polyenyl cations, irrespective of the dehydrochlorination mechanism. In the subsequent step, however, which consists in the termination of hydrogen chloride elimination by splitting-off of hydrogen, the reaction may be controlled by two alternative factors. In the case of radical mechanism reactivity of the polyenyl radical is still affected by the remaining charge potential. On the contrary, the fate of the polyenyl cation is influenced by the magnitude of partial charge on the π-electron conjugated system. With increasing polyene sequence the value of this charge is distributed through a longer unsaturated system. It may be assumed, therefore, that the splitting-off of the hydrogen atom will be increasingly more impeded, until eventually it will be stopped. Thus, the propagation of polyene is spontaneously terminated.

When studying properties of polymers using low-molecular weight models, one should always bear in mind whether the size of the selected systems adequately describes the real behaviour of the polymer. A discussion of the individual Tables, balances of the particular mechanisms, and spectral values reveal that the basic limits are already very well reflected with C_7 systems, while systems C_9, C_{11} confirm the suggested trends quite unambiguously. An unequivocal result is that also on short C_5, C_7 skeletons the ratios of partial charges are in a very good agreement with more extensive systems.

CONCLUSIONS

The semiempirical quantum chemical MNDO method has been applied in a description of the gradual dehydrochlorination of syndiotactic oligomers of vinyl chloride, ranging from dimer to pentamer. The results obtained lead to the following conclusions:

1) The chloropropenyl group, formed by the elimination of the first hydrogen chloride molecule from the originally saturated system, facilitates by activation further dehydrochlorination steps, while giving rise to polyene sequences.

2) The chloroallyl and repeated α-chloropolyene activations can be considered as a consequence of the existing charge potential $\mu(C^{\omega} - C^{\alpha})$, which is formed at the edge between the unsaturated and saturated part of the chain, C^{ω} being the end carbon atom of the unsaturated system, C^{α} being the carbon atom of the –CHCl– group in the α-position to the π-electron system.

3) The propagation stage of dehydrochlorination is a result of the repeatedly formed charge potential $\mu(C^{\omega} - C^{\alpha})$; it proceeds by the radical and/or ionic mechanism depending on the reaction conditions and environment surrounding the reaction sites. It may be assumed that during propagation, in dependence on the polyene length, the radical mechanism changes to the ionic one.

4) The charge distribution symmetry of the π-electron system suggests that the resonance structures are formed in reaction intermediates of the polyenyl-radical and polyenyl-cation types. This fact results in the same probability of propagation of the polyene in both directions from the initiation site along the polymer chain, i.e. the dehydrochlorination on the PVC chain proceeds by the "alternation growth" mechanism.

5) In the case of the ionic mechanism it was shown that propagation of the polyenes may be accompanied by a spontaneous termination.

6) Calculations carried out using variously extensive systems indicate that sufficiently exact results can be achieved already with C_7 systems.

REFERENCES

1. Lukáš R.: Makromol. Chem., Macromol. Symp. *29*, 21 (1989).
2. Lukáš R., Přádová O.: Makromol. Chem. *187*, 2111 (1986).
3. Milan J.-L., Martinez G., Gómez-Elvira J. H.: Makromol. Chem., Macromol. Symp. *29*, 185 (1989).
4. Dewar M. J. S., Thiel W.: J. Am. Chem. Soc. *99*, 4899, 4907 (1977).
5. Lukáš R.: *Proc. 2nd AKZO Inter. Symp. "PVC and Initiators", Singapore 1990;* Chapter 11, p. 1 (1990).
6. Chytrý V., Obereigner B., Lím D.: Eur. Polym. J., Suppl. *1969*, 379.
7. Obereigner B.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1973.
8. Lukáš R., Toman L.: Polym. Bull. (Berlin) *24*, 277 (1990).
9. Lukáš R., Toman L.: Polym. Bull. (Berlin) *24*, 285 (1990).

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