DEHYDROCHLORINATION OF POLY(VINYL CHLORIDE) IN ISOTACTIC SYSTEMS*

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The dehydrochlorination of isotactic, low-molecular-weight models of PVC, dimers to pentamers, was studied using the semiempirical MNDO method. The results obtained lead to the conclusion that the thermal dehydrochlorination of PVC can occur through either a radical or an ionic mechanism, depending on the reaction conditions. The arising conjugated polyene structures do not grow by the generally accepted "zip" mechanism, but rather through the "alternating growth" mechanism. A comparison was also made of the reactivity of isotactic and syndiotactic sequences from the point of view of kinetic and thermodynamic factors. It follows from the computations that the splitting off of the first HCl molecule is easier in the isotactic sequence, but that subsequent growth of the polyene chain occurs more readily in syndiotactic systems.

The previous work[1] dealt with a theoretical study of the thermal dehydrochlorination of syndiotactic sequences of poly(vinyl chloride). The MNDO semiempirical quantum-chemical method was first applied to saturated low-molecular-weight models, vinyl chloride dimers to pentamers, and to their unsaturated derivatives containing 1 to 4 conjugated double bonds. In the second part of this work[1], a study was focussed on the estimation of the behaviour of corresponding radical and ionic intermediates formed in the individual dehydrochlorination steps by the detachment of the chlorine as a radical or anion. The results obtained permitted the formulation of the following conclusions:

a) Activation of allylic and α-chloropolyene chlorine in the dehydrochlorination is a consequence of the formation of a charge potential $\mu(C^{\omega} - C^{\alpha})$ between the unsaturated and saturated parts of the chain (C^{ω} being the terminal carbon atom in the unsaturated system and C^{α} the carbon atom of the –CHCl– group located in the α-position with respect to the π-electron system);

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b) Propagation phase of the dehydrochlorination controlled by repeatedly formed charge potential $\mu(C^{\omega} - C^{\alpha})$ proceeds in dependence on the reaction conditions and length of the polyene by radical or ionic mechanism;

c) As a consequence of the symmetry of the charge distribution in the reaction intermediates of the polyenyl radical or polyenyl cation type, the propagation and thus the growth of conjugated polyene do not proceed from the initiation site through the "zip" mechanism, but rather through the "alternating growth" mechanism, i.e. the polyene grows from the initiation site in both directions along the polymer chain with the same probability;

d) In the ionic mechanism, the propagation phase is accompanied by spontaneous termination.

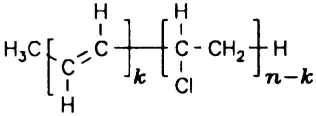
These findings published earlier, together with the experimental results[2 – 4] permit the reevaluation of contemporary knowledge on the mechanism of PVC thermal dehydrochlorination and stabilization. However, the literature also contains experimental data[5] describing the effect of tacticity of the polymer chain on the splitting off of hydrogen chloride and, therefore, this work complements our study on predicting the mechanism of thermal dehydrochlorination in isotactic PVC sequences.

CALCULATIONS

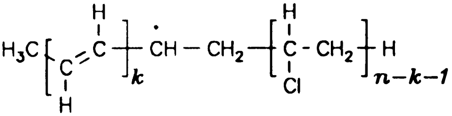
Saturated isotactic PVC sequences were studied using vinyl chloride oligomer models, dimer to pentamer, viz. 2,4-dichloropentane (*I*, $n = 2$, $k = 0$), 2,4,6-trichloroheptane (*I*, $n = 3$, $k = 0$), 2,4,6,8-tetrachlorononane (*I*, $n = 4$, $k = 0$) and 2,4,6,8,10-pentachloroundecane (*I*, $n = 5$, $k = 0$), where *n* denotes a given oligomer and *k* is a number of double bonds in conjugation. The unsaturated derivatives (*I*, $n = 2 – 5$, $k \neq 0$), formed by a gradual splitting off of hydrogen chloride from the saturated models, were modelled with trans configuration on the double bonds. For consistency with ref.[1], the MNDO semiempirical method[6] with complete optimization of the geometry of the individual models was employed for the study. In contrast to syndiotactic systems, where the trans-trans conformation diad structure is energetically most favourable, the behaviour of the isotactic sequence was studied using the more stable trans-gauche' diad conformation[7].

Reaction intermediates formed in dehydrochlorination steps were also investigated. The chlorine was split off both as a radical (homolytic splitting of the C–Cl bond) and also as chloride anions (heterolytic splitting). The intermediates were also subjected to complete geometry optimization.

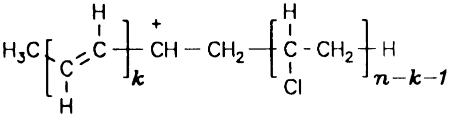
In formulae *I*, *II* and *III*, rotated Fischer projection was used.



I



II



III

RESULTS AND DISCUSSION

Elimination of Hydrogen Chloride

In optimized saturated and unsaturated C_5 – C_{11} models, the energy balance was first determined for the process of elimination of HCl molecules, as described by Eq. (*A*),

$$I(n, k) \rightarrow I(n, k + 1) \tag{A}$$

The resulting energy balance of the reaction is summarized in Table I. It can be seen that, similarly as for the syndiotactic PVC sequence, the growth of the polyene structure in the isotactic chain is also not an exothermic process. However, the absolute value of the energy connected with the elimination of hydrogen chloride is somewhat lower than for the syndiotactic sequence and equals approx. 50 kJ mol^{-1}.

Subsequent comparison of the energy levels of the HOMO and LUMO frontier orbitals is given in Table II. It follows from Table II that the energies of the studied MO do not exhibit such a great similarity as for the syndiotactic system[1]. However, the "vertical behaviour" of the eigenvalues of the HOMO/LUMO frontier orbitals[1] is still apparent, documenting that the predominant properties of the studied systems are characterized by the π-electron system. It follows from detailed analysis of the wave vectors that this behaviour is connected with the character of the corresponding molecular orbitals, as was discussed in the previous work[1]. If the magnitudes of the HOMO and LUMO energies given in Table II for the C_9, C_{11} and partly also for the C_7 systems are compared with the magnitudes of the energies of the analogous syndiotactic structures (Table II, ref.[1]), then it is found that the HOMO/LUMO energies of the unsaturated isotactic sequences are always lower, especially when the structure contains only one or two double bonds. This finding is interesting from a kinetic point of view as it permits assumption that isotactic systems seem to be more stable than the corresponding syndiotactic systems in both the monomolecular and the bimolecular mechanism of dehydrochlorination catalyzed by an additional hydrogen chloride molecule (HOMO

TABLE I
Energy balances (eV) of dehydrochlorination of *I* by reactions *A*, *B* and *C*

n	Change in *k*	E_A	E_B	E_C
2	0 → 1	0.55	2.61	6.74
	1 → 2	–	2.64	5.69
3	0 → 1	0.53	2.60	6.84
	1 → 2	0.53	2.53	5.77
	2 → 3	–	2.65	5.24
4	0 → 1	0.53	2.59	6.88
	1 → 2	0.51	2.52	5.84
	3 → 4	–	2.63	4.87
5	0 → 1	0.52	2.59	6.91
	1 → 2	0.50	2.52	5.87
	2 → 3	0.50	2.50	5.29
	3 → 4	0.52	2.53	4.82
	4 → 5	–	2.66	4.67

TABLE II
LUMO and HOMO energies (eV) of *I*

n	*k* = 0	*k* = 1	*k* = 2	*k* = 3	*k* = 4
2	0.44	0.15	–	–	–
	−12.07	−10.20	–	–	–
3	0.28	−0.05	−0.31	–	–
	−12.12	−10.37	−9.29	–	–
4	0.15	−0.15	−0.46	−0.58	–
	−12.12	−10.44	−9.42	−8.82	–
5	0.10	−0.19	−0.53	−0.71	−0.57
	−12.11	−10.48	−9.48	−8.92	−8.64

and LUMO energies ≈ −13.01 and 0.92 eV, respectively). Consequently, the chain dehydrochlorination of the isotactic sequences should proceed more slowly. This conclusion explains the experimentally determined fact[5] that polyenes grow less readily in isotactic sequences than in syndiotactic sequences.

Mulliken analysis of the systems studied yielded the distribution of the electron densities on the individual atoms. A picture of the distribution of the partial charge on the carbon atoms can be obtained from Fig. 1, depicting the saturated C_{11} system, I, $n = 5$, $k = 0$ and structures I, $n = 5$, $k = 2$ and I, $n = 5$, $k = 4$ with two and four conjugated double bonds, respectively. The partial charge on the carbon atoms of the unsaturated conjugated system should be symmetrically distributed. However, it follows from Fig. 1 that the calculated distributions are unsymmetrical, e.g. compared to the magnitude of the boundary minima. This fact is connected with the choice of a computational model and is a consequence of the chemically different substituents at the ends of the π-electron system, as discussed in the previous work[1]. In addition, the conclusions on the charge resonance[1] remain valid: the occurrence of partial negative charge maxima on the boundary carbon atoms of the π-conjugated system, and also the constant magnitude of the charge potential $\mu(C^{\omega} - C^{\alpha})$ between the terminal negatively charged carbon of the π-conjugated system C^{ω}, where charge is cumulated, and the subsequent strongly positive partial charge on the C^{α} carbon atom substituted by an electronegative chlorine atom. It is apparent from comparison of the individual systems, dehydrochlorinated to various degrees (I, $n = 5$, $k = 2$ and I, $n = 5$, $k = 4$; Fig. 1), that the increasing π-electron conjugated system does not affect the magnitude of the $\mu(C^{\omega} - C^{\alpha})$ interaction.

Dehydrochlorination Mechanism

This part of work describes investigation of the mechanism of the activation by allylic and α-chloropolyenyl chlorine of the propagation phase of the dehydrochlorination of the isotactic PVC sequences. It is considered whether the dehydrochlorination occurs

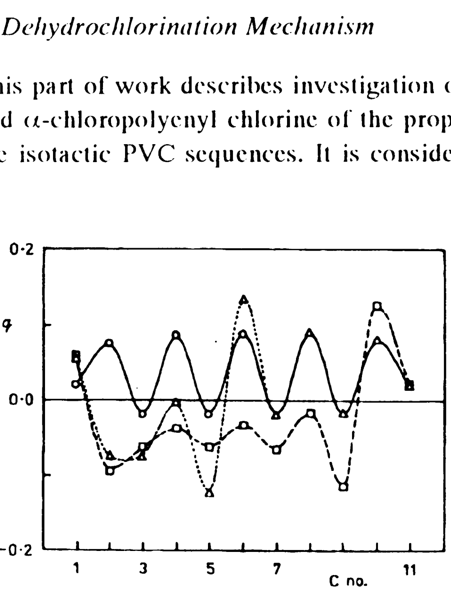


FIG. 1
Distribution of the partial charge on the carbon atoms in I, $n = 5$; ○ $k = 0$, Δ $k = 2$, □ $k = 4$

preferentially through the radical or ionic mechanism. Thus, the elimination of hydrogen chloride was divided into two reaction steps consisting of detachment of the chlorine particle and then completing the HCl elimination by the detachment of hydrogen (Eqs (*B*) and (*C*)):

$$I \xrightarrow{-\mathrm{Cl}^{\bullet}} II \qquad (B)$$

$$I \xrightarrow{-\mathrm{Cl}^{-}} III \qquad (C)$$

For consistency with the previous results[1], the detached chloride anion was considered in the energetically more stable form, HCl_2^-. In modelling the intermediates in the elimination of hydrogen chloride from the isotactic diad (trans-gauche') sequence, optimization of these intermediates involves the formation of a cis arrangement on the carbon, from which the chlorine is detached (the value of the torsion angle on this carbon changes from 60° (gauche) to 0° (cis)). However, this form has higher energy than the trans form*.

The resultant energies of processes (*B*) and (*C*) are listed in Table I. It follows from comparison that the energies connected with the formation of a radical transition state are much lower than the corresponding energies of the ionic transition state. Thus, if there are no polar interactions that would favour the ionic mechanism, the radical mechanism of splitting of the C–Cl bonds should predominate. Figure 2 depicts the dependences of the activation energy for both mechanisms of the detachment of the chlorine on the number of conjugated double bonds in the C_{11} system and, for comparison, also the results for the syndiotactic sequence. Compared with the ionic mechanism, the activation energies for radical propagation are almost constant, regardless of the number of conjugated double bonds in the system. It can also be clearly seen that these activation energies for the detachment of chlorine as a radical are lower for the isotactic than for the syndiotactic systems (Fig. 2). In the ionic mechanism there is a clear dependence of the activation energy on the length of the π-electron system of the chain (Fig. 2) and it is apparent from the shape of the curves that there is a limit value of the activation energy for the detachment of the chloride ion, to which a sufficiently long π-electron system converges. This dependence was discussed in ref.[1].

It follows from the above paragraph that in the dehydrochlorination by the radical mechanism (which is assumed at least in the initial stage[1]) the elimination of the HCl

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* The formation of the cis arrangement is connected only with the rigid model of the structure of the initial optimized system. However, because real system undergoes various vibrational and rotational motions, it has time to take the most favourable geometric arrangement, i.e. here trans. Consequently, in subsequent computations the initial structure with the trans conformation on the carbon was employed.

molecule should occur more readily in the isotactic sequence, judged from a thermodynamic point of view on the reaction coordinate profile.

As the HOMO orbital energies of the model systems of the two stereoisomers are very similar for saturated chains (Table II and analogous Table II in ref.[1]), it can be expected that kinetic factors will not be important in the first stages of the initiation. It can thus be concluded that the elimination of the first molecule of hydrogen chloride occurs more readily in the isotactic sequence.

The energy values of the frontier orbitals of the radical intermediates are given in Table III. It can be seen that, compared with the radicals of the syndiotactic systems, the energies of the SOMO orbitals are lower, which predicts that the radicals with

TABLE III
LUMO, SOMO and HDOMO energies (eV) of *II*

n	*k* = 0	*k* = 1	*k* = 2	*k* = 3	*k* = 4
2	0.76	1.42	–	–	–
	-4.57	-4.31	–	–	–
	-11.99	-10.48	–	–	–
3	0.48	0.76	0.60	–	–
	-4.71	-4.59	-4.34	–	–
	-12.04	-10.76	-9.29	–	–
4	0.30	0.49	0.37	0.08	–
	-4.77	-4.69	-4.57	-4.37	–
	-12.11	-10.85	-9.76	-8.82	–
5	0.17	0.31	0.27	-0.09	-0.26
	-4.82	-4.73	-4.65	-4.54	-4.38
	-12.11	-10.88	-9.84	-9.15	-8.60

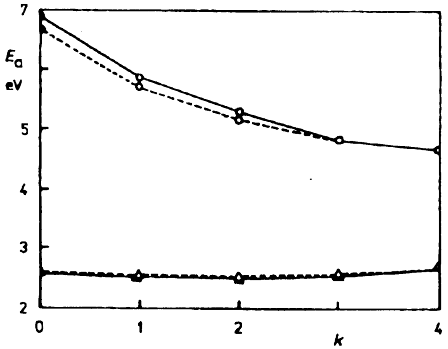

FIG. 2
Dependence of the activation energy of chlorine detachment in *I*, *n* = 5 on the number of conjugated double bonds, *k*; Δ radical mechanism, ○ ionic mechanism, —— isotactic model, - - - syndiotactic model

isotactic conformation will be kinetically less reactive. Consequently, the subsequent detachment of the hydrogen atom should be faster for the syndiotactic sequence. Thus, the final mechanism will depend on which factor will be more important in comparison of the stereoisomers – the difference in the activation energies or the difference in the frontier orbital energies.

In the ionic mechanism of elimination of HCl, it follows from comparison of Tables II in this and the previous work[1] that the activation energy is lower for the syndiotactic chain conformation. The frontier orbital energies, given for the ionic system in Table IV, are not so unambiguous for the reactivity prediction as those given in the analogous Table IV for the syndiotactic system[1], as found for both the basic systems and the radical intermediates. However, as both the thermodynamic approach (activation energy) and the point of view derived from the frontier orbital energies of the basic systems are in agreement, it follows that, in case of the ionic mechanism of dehydrochlorination, the chloride anion will be detached from the syndiotactic sequence also more readily than from the isotactic system.

In Tables III and IV, the "diagonal" similarity of the SOMO orbitals of radicals and the "vertical" similarity of the LUMO orbitals of the ionic systems do not follow as unambiguously as for the syndiotactic systems[1]. This is because of the greater scatter of the frontier orbital energies. However, a clear dependence of the orbital energy on the number of double bonds in the LUMO of radicals and HOMO and LUMO-1 of cation intermediates, as discussed in ref.[1], remains.

TABLE IV
LUMO-1, LUMO, and HOMO energies (eV) of *III*

n	*k* = 0	*k* = 1	*k* = 2	*k* = 3	*k* = 4
2	-3.59	-4.52	–	–	–
	-8.21	-7.39	–	–	–
	-15.95	-16.20	–	–	–
3	-3.73	-4.61	-4.35	–	–
	-8.29	-7.48	-6.88	–	–
	-14.86	-15.28	-14.37	–	–
4	-3.80	-4.66	-4.46	-4.29	–
	-8.33	-7.54	-6.99	-6.52	–
	-14.25	-14.51	-14.44	-13.23	–
5	-3.83	-4.69	-4.50	-4.30	-4.24
	-8.35	-7.57	-7.04	-6.53	-6.25
	-13.78	-14.07	-14.26	-13.25	-12.44

It can be seen in the above discussion that there is a connection between the mechanism of detachment of the chlorine or hydrogen and the ratio of the eigenvalues of the HOMO or SOMO for both the stereoisomers and their derivatives formed through the elimination of hydrogen chloride. The quality of the difference Δe[HOMO(iso) − HOMO(syndio)] for the basic systems and Δe[SOMO(iso) − SOMO(syndio)] for radicals (Table V) is also retained in the homolytic splitting of the C–Cl bond, where the driving force remains the charge potential[1] $\mu(C^{\omega} - C^{\alpha})$. From a quantitative point of view, there is an ever greater difference between the iso- and syndiotactic structures for radicals derived from the saturated models, even though the basic systems do not exhibit any great difference between these two structures. This difference compared to the saturated models is a consequence of the formation of sp^2 hybridization on the carbon at which the C–Cl bond is split, connected with the formation of a SOMO orbital through the p_z atomic orbital freed from hybridization. The difference between the isotactic and syndiotactic structures is to be found in these π-electrons. This difference decreases with increasing length of the π-electron system.

However, in the ionic mechanism, the charge potential $\mu(C^{\omega} - C^{\alpha})$ acting as a driving force for the dehydrochlorination is replaced by alternating electron density with approximate localization of the partial positive charge in the centre of the π-conjugated system. Electrostatic forces are more important here; and, from the point of view

TABLE V

Energy differences (eV) of the frontier molecular orbitals[a] between the isotactic and syndiotactic systems ($e_{iso} - e_{syndio}$)

n	System	*k* = 0	*k* = 1	*k* = 2	*k* = 3	*k* = 4
2	*I*	0.0	0.0	–	–	–
	II	0.15	0.0	–	–	–
	III	-0.34	0.0	–	–	–
3	*I*	0.0	0.11	0.0	–	–
	II	0.23	0.17	0.0	–	–
	III	-0.03	-0.31	0.0	–	–
4	*I*	0.0	0.13	0.08	0.0	–
	II	0.28	0.22	0.14	0.0	–
	III	0.12	-0.02	0.07	0.0	–
5	*I*	0.0	0.16	0.11	0.06	0.0
	II	0.32	0.25	0.19	0.10	0.0
	III	0.10	0.17	0.02	0.01	0.0

[a] HOMO for *I* and *III*, SOMO for *II*.

of the reactivity, they predominate over the smaller effect of the frontier orbitals[8] and, in the framework of the SCF approach, considerably affect them (Table V).

CONCLUSIONS

Computations carried out on the oligomer models of isotactic PVC lead to the conclusion that the thermal dehydrochlorination of the isotactic sequence is controlled by the same factors as in the dehydrochlorination of the syndiotactic segments, and thus occurs in a similar manner.

Interesting predictions follow from the comparison of the mechanism of the dehydrochlorination in the two studied stereoisomeric sequences of the PVC chain. Considering the initiation step of dehydrochlorination through detachment of chlorine from the intact saturated chain, it follows that, as a consequence of the same energy ratios in the frontier orbitals, it can be expected for thermodynamic reasons (lower activation energy) that the chlorine radicals will be more readily detached from the isotactic sequence. If the system undergoing dehydrochlorination already contains conjugated double bonds, then the dehydrochlorination is dependent on the reaction mechanism. For the ionic mechanism of dehydrochlorination, the reaction occurs more readily in the syndiotactic sequences. For the radical mechanism, then the greater effect of the frontier orbitals favours faster dehydrochlorination through the isotactic sequence, although not as unambiguously as for the ionic mechanism. This ambiguity as to the dehydrochlorination process can be eliminated by correlation with the experimental data[5], confirming the easier initiation in the isotactic sequences, but easier propagation of dehydrochlorination in syndiotactic sequences. It can thus be expected that the dehydrochlorination of PVC segments occurs initially through the radical mechanism, which gradually changes to the ionic mechanism. This concept successfully interprets the controversial published results, which demonstrate both the stabilizing effect of additives with the properties of radical scavengers as well as a dependence of the dehydrochlorination on the polarity of the medium. The growth of the polyene through the ionic mechanism leads to a spontaneous termination because the weakening alternation of the partial charge of the polyenyl cation slows down the detachment of proton. The growing polyene is thus terminated at the level of the onium salt polyenyl$^{(+)}$ Cl$^{(-)}$, which is also responsible for the discolouration of the polymer. The consequences of these concepts for the stabilization of PVC will be considered in the next work.

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